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Methodology Study of *N*-deacetylation of 4-acetamido-perfluoroalkylbenzenesulfonimide

A thesis
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfilment
of the requirements for the
Master of Science in Chemistry

by
Grace Abban
August 2015

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Keywords: *N*-deacetylation, perfluoroalkyl benzenesulfonylimide (PFSI) monomer

ABSTRACT

Methodology Study of *N*-deacetylation of 4-acetamido-perfluoroalkylbenzenesulfonimide

by

Grace Abban

In order to improve the synthetic route for diazonium perfluoroalkyl benzenesulfonylimide (PFSI) zwitterionic monomers, *N*-deacetylation of the coupling product was proposed to replace the reduction of aromatic amine intermediates. A series of hydrolysis methods, such as acid and base catalyzed refluxing, were explored for the *N*-deacetylation to obtain the PFSI aromatic amine. Factors such as temperature, concentration of acid/base and the time needed for the reaction to take place were investigated in an attempt to optimize the reaction condition. The basic hydrolysis was preferred since it was expected to carry out the *N*-deacetylation and debromination in one batch reaction. *N*-deacetylation in base at high concentrations was successful, however, side reaction of the perfluorovinyl ether occurred. It was discovered that the best *N*-deacetylation method is to reflux/sonicate the coupling product with acid in methanol for six hours. The intermediates and purified products were characterized with ^1H NMR, ^{19}F NMR, GC-MS and IR.

DEDICATION

This work is dedicated to the Almighty God for his protection and guidance, my father Mr. Joseph Abban, my mother madam Anastasia Donkoh and my siblings.

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Thanks to God Almighty for his protection, care, abundant grace and mercy that has seen me through my course successfully. My sincere gratitude goes to my advisor Dr. Hua Mei for her guidance and encouragement throughout this research work, I say God richly bless you.

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TABLE OF CONTENTS

	Page
ABSTRACT	2
DEDICATION	3
ACKNOWLEDGEMENTS	4
LIST OF FIGURES	8
LIST OF SCHEMES	9
LIST OF ABBREVIATIONS	10
Chapter	
1. INTRODUCTION	11
Preface	11
<i>N</i> -deacetylation	11
Fuel Cells	17
Diazonium PFSI Zwitterionic Monomers.....	20
2. RESEARCH AND DISCUSSION	25
Ammonolysis Reaction of 4-Sulfamonylacetanilide	25
Bromination of Nafion [®] Monomer	26
Coupling Reaction	26
<i>N</i> -deacetylation of the Coupling Product	28
3. EXPERIMENTAL	35
General Considerations	35

Chapter	Page
NMR Spectroscopy	35
Gas Chromatography-Mass Spectrometer	35
Infra-Red Spectroscopy	35
Glass Vacuum System	36
Thin Layer Chromatography	36
Purification of Solvents and Experimental Practice	36
Synthesis of 4-sulfamonylacetanilide	37
Synthesis of $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$	37
Synthesis of $\text{CH}_3\text{CONHPhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$	38
Synthesis of $\text{NH}_2\text{PhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$	39
Synthesis of $\text{NH}_2\text{PhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$	40
4. CONCLUSION	41
REFERENCES	43
APPENDICES	47
Appendix A: GC-MS Chromatogram of Compound 2	47
Appendix B1: ^{19}F NMR Spectrum of Compound 3 , 400MHz, Acetone- d_6	48
Appendix B2: ^{19}F NMR Spectrum of Compound 4 , 400MHz, CD_3CN	49
Appendix B3: Expanded ^{19}F NMR Spectrum of Compound 4 , 400MHz, CD_3CN	50
Appendix B4: ^{19}F NMR Spectrum of Compound 5 , 400MHz, CD_3CN	51

Chapter	Page
Appendix B5: ^{19}F NMR Spectrum of Compound 6 , 400MHz, CD_3CN	52
Appendix B6: ^{19}F NMR Spectrum of Compound 6' , 400MHz, CD_3CN	53
Appendix B7: ^{19}F NMR Spectrum of Basic Hydrolysis Byproduct, 400MHz, CD_3CN ..	54
Appendix C1: ^1H NMR Spectrum of Compound 1 , 400MHz, Acetone- d_6	55
Appendix C2: ^1H NMR Spectrum of Compound 2 , 400MHz, CD_3CN	56
Appendix C3: Expanded ^1H NMR Spectrum of Compound 2 , 400MHz, CD_3CN	57
Appendix C4: ^1H NMR Spectrum of Compound 5 , 400MHz, CD_3CN	58
Appendix C5: Expanded ^1H NMR Spectrum of Compound 5 , 400MHz, CD_3CN	59
Appendix C6: ^1H NMR Spectrum of Compound 6 , 400MHz, CD_3CN	60
Appendix C7: Expanded ^1H NMR Spectrum of Compound 6 , 400MHz, CD_3CN	61
Appendix D1: FT-IR Spectrum of Compound 1	62
Appendix D2: FT-IR Spectrum of Compound 2	63
Appendix D3: FT-IR Spectrum of Compound 5	64
Appendix D4: FT-IR Spectrum of Compound 6	65
VITA	66

LIST OF FIGURES

Figure	Page
1. The structure of the leaving group.....	12
2. The structure of the PEM fuel cell (modified from Thampan).....	19
3. The possible hydrolysis by-product from the coupling reaction	27
4. The structure of the protonated amide tetrahedral adduct	33
5. The structure of the debrominated product	34
6. The line diagram of the dual-manifolds glass vacuum line. Used with permission	36

LIST OF SCHEMES

Scheme	Page
1. The resonance structure of the PFSI monomer.....	12
2. An example of an acid catalyzed amide hydrolysis.....	13
3. The mechanism for the acid catalyzed <i>N</i> -deacetylation	14
4. The base catalyzed hydrolysis mechanism	16
5. The reactions occurring in a PEM fuel cell.....	19
6. An example of an amino acid zwitterion	20
7. The grafting of the FDZ on the carbon electrode.....	21
8. The previously published overall synthesis scheme.....	22
9. The proposed synthesis scheme	23
10. The ammonolysis reaction of <i>N</i> -acetyl sulfanilyl chloride	25
11. The bromination reaction of Nafion [®] monomer	26
12. The coupling reaction of 4-sulfamonylacetanilide with brominated Nafion [®] monomer	27
13. The <i>N</i> -deacetylation reaction of the coupling product	32

LIST OF ABBREVIATIONS

AFC	Alkaline Fuel Cell
DIEA	Diisopropyl Ethyl Amine
DIEAH ⁺	Diisopropyl Ethyl Amine Salt
DMFC	Direct Methanol Fuel Cell
FDZ	Functional Diazonium Zwitterion
FT-IR	Fourier Transform Infra-Red
GC-MS	Gas Chromatography-Mass Spectrometry
Hz	Hertz
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
NMR	Nuclear Magnetic Resonance
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PFSA	Perfluorosulfonic acid
PFSI	Perfluorosulfonylimide
ppm	Parts per million
SOFC	Solid Oxide Fuel Cell
TMS	Tetramethylsilane
TLC	Thin Layer Chromatography
UV	Ultra Violet

CHAPTER 1

INTRODUCTION

Preface

This research was aimed at the methodological study of *N*-deacetylation of 4-acetamido-perfluoroalkylbenzenesulfonimide to replace the reduction of nitroaromatics in the synthetic route of diazonium perfluoroalkyl benzene sulfonimide (PFSI) zwitterionic monomers for use in proton exchange membrane (PEM) fuel cells after polymerization.

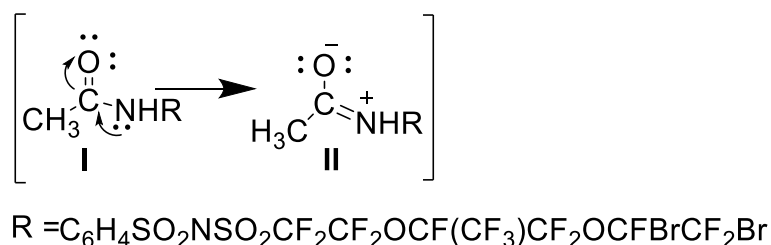
Background for this project, along with the motivation of this research work, is given in the introduction. The details about this methodological study, as well as the characterization of both the intermediates and products, are discussed in the subsequent chapters. *N*-deacetylation is presented first, followed by a short overview of fuel cells, and finally an overview of the recently synthesized diazonium PFSI zwitterionic monomers. The use of acetamide was expected to expedite both the ammonolysis and coupling reactions. Also, the inorganic impurity associated with the aromatic reduction can be avoided with the new method.

N-deacetylation

N-deacetylation, also known as the hydrolysis of amides, is a nucleophilic acyl substitution reaction which occurs via an addition-elimination mechanism.¹ It is a very effective synthesis method to produce amines.² For organic synthesis design, amines are often protected since they are very active groups, which are prone to be further oxidized, or undergo electrophilic aromatic substitution.³ The main factors that affect the reactivity of amide hydrolysis include: 1) resonance stability, 2) leaving group ability and 3) steric effect.⁴

The resonance structure (**II** in Scheme 1) of the PFSI aromatic acetamide is destabilized by the electron-withdrawing perfluoroalkyl chain. The loss of the resonance stability of the PFSI

aromatic acetamide results in a lower transition state energy. Therefore, the reactivity of the PFSI aromatic acetamide towards nucleophiles is expected to be higher than regular aromatic acetamide.



Scheme 1: The resonance structure of the PFSI monomer.

As shown in Figure 1 below, the perfluoroalkyl group also balances the negative charge of the leaving group in the hydrolysis. This leads to a much faster reaction towards nucleophilic substitution reactions.⁴ The reactivity of the *N*-deacetylation of PFSI acetamide aromatic compound is again expected to be better than for regular aromatic acetamide.

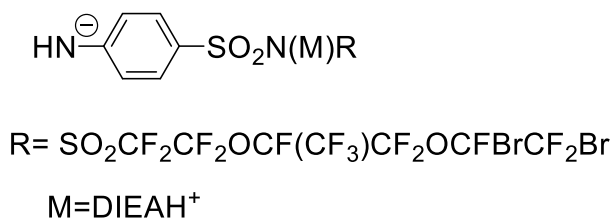


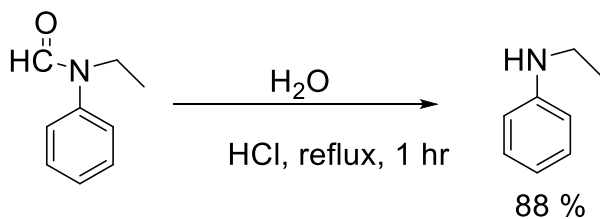
Figure 1: The structure of the leaving group.⁴

Meanwhile, the nucleophilic attack on the PFSI aromatic acetamide may be blocked by the bulky aromatic PFSI section, which may slow down the hydrolysis reaction.⁴

Since there are conflicts with the three factors, the exploration of the deacetylation of PFSI aromatic acetamide is crucial to study. Water, as a weak nucleophile, will be used with an acid or base catalyst.

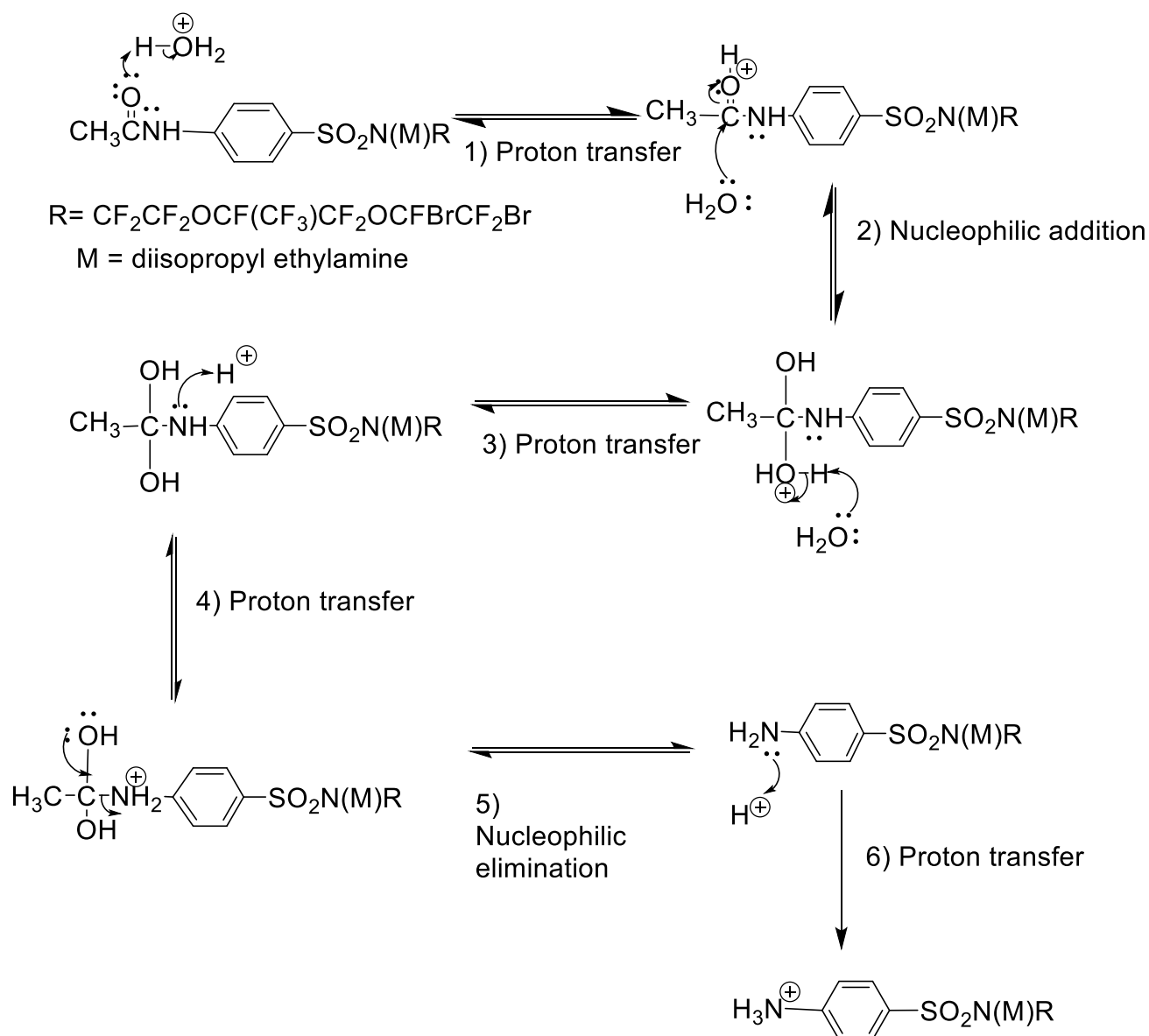
Generally, there are two types of traditional methods for the hydrolysis of amides. The first one is the acid catalyzed hydrolysis, which is carried out mostly in strong acids under reflux

conditions for a long time.⁶ An example of an acid that is used for the acid catalyzed hydrolysis is hydrochloric acid under reflux.⁶



Scheme 2: An example of an acid catalyzed amide hydrolysis.⁶

The mechanism starts with protonation of the carbonyl (C=O) to form a better electrophile, which facilitates the nucleophilic attack by the weak nucleophile in the next step. The proton transfer occurs in the 3rd and 4th steps after the addition of the water (H₂O). And then, the amide will undergo elimination to expel the amine, which abstracts a proton from the acid again in order to form the ammonium salt. The desired amine product is obtained after neutralization.

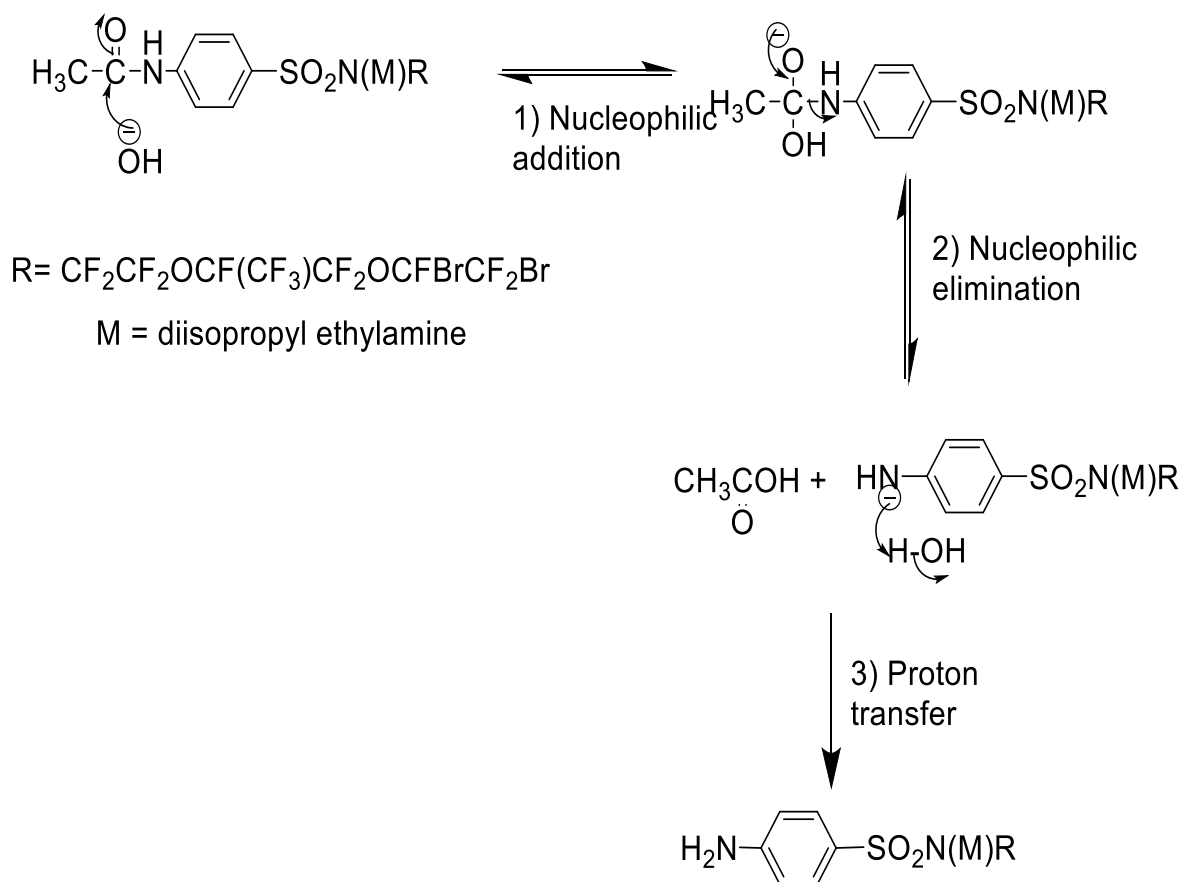


Scheme 3: The mechanism for the acid catalyzed *N*-deacetylation.

Usually the catalysts used for the acid hydrolysis are strong mineral acids, Lewis acids or Brønsted acids under reflux conditions. Recently, examples of methods studied for the acid hydrolysis catalysts include: H_2 and MeSO_3H in THF under autoclave,⁶ Hydrozirconocene Cl in THF⁷ at room temperature, SOCl_2 in MeOH,⁹ and AlCl_3 ¹¹ under microwave irradiation. These methods were used to prepare primary,⁶ secondary and tertiary amines such as *N*-butylamine, *N*-

ethylaniline and tributylamine respectively. Also there is no C-N bond cleavage⁷ from the hydrolysis of aromatic amides and heteroaromatic amides. The above methods are clean, solvent free and result in high yields of the desired products.^{11, 12} Furthermore, there is no observable epimerization of chiral acetamides associated with these methods.⁷ However, harsh conditions, costly catalysts and long reaction times are required to carry out such reactions.¹³ Moreover, problems like low chemical selectivities,²¹ and formation of the corresponding carboxylic acids or esters^{10, 22} are associated with some methods.

The second type of methods involves reflux with strong base. The base catalyzed hydrolysis mechanism is different from the acid mainly in the first step. The acid catalyst is employed to generate a stronger electrophile while the base catalyst converts water into a strong nucleophile, the hydroxyl anion. The base hydrolysis amide mechanism starts with the nucleophilic addition of the base, followed by the nucleophilic elimination of the leaving-group and next the abstraction of a base to form the desired amines as shown in Scheme 4.



Scheme 4: The base catalyzed hydrolysis mechanism.

Generally the catalysts used for the base hydrolysis are strong Lewis bases or Brønsted bases. Up-to-date research explored all kinds of base hydrolysis catalyst conditions, such as: NaOH in H₂O and ETOH,⁵ N₂H₄-H₂O with NH₄I,⁵ NH₄Br and H₂NCH₂CH₂NH₂,⁵ and KF on alumina catalyst¹² all under microwave irradiation and C₅H₅N in ClCH₂CH₂Cl⁸ at room temperature. These methods are compatible with a wide range of functional groups such as carboxylic acids, phenols and indoles.⁵ Similarly, they can be used with an extensive variety of acylated amines.⁵ However, harsh conditions, costly catalysts and long reaction times are again needed.

Fuel Cells

Fuel cell technologies have received much attention over the years as the means of providing viable clean energy, due to the growing concerns about the depletion of petroleum energy resources and climate change. Although hydrogen is the most common fuel, hydrocarbons such as natural gas and alcohols like methanol are sometimes used for greater efficiency.¹⁴ Fuel cells have the likelihood of replacing the internal combustion engine in vehicles and other power applications due to their energy-efficient, clean and fuel flexibility characteristics.^{16, 19} Fuel cells batteries are different from regular batteries because fuel cells require a constant source of fuel and oxygen/air to sustain the chemical reaction. Fuel cells can produce electricity continually for as long as these inputs are supplied. The applications of fuel cells include power for transportation, portable power generation and stationary power generation.¹⁵ A fuel cell consists of an electrolyte that is enfolded between two electrodes (cathode and anode) to generate electricity.¹⁶ To produce electrical current, the electrons move from the anode to the cathode through an external circuit.

Table 1:¹⁶⁻¹⁸ Comparison of different types of fuel cells.

Fuel Cell	Electrolyte	Fuel Used	Operating Temperature
Polymer Electrolyte Membrane Fuel Cell (PEMFC)	H ⁺ conducting Membrane	H ₂	~80 °C
Alkaline Fuel Cell (AFC)	KOH	H ₂	~100 °C
Phosphoric Acid Fuel Cells (PAFC)	Concentrated H ₃ PO ₄	Natural gas, H ₂	~200 °C

Table 1 (continued)

Molten Carbonate Fuel Cells (MCFC)	Molten K_2CO_3	Natural gas, H_2	~650 °C
Solid Oxide Fuel Cell (SOFC)	Zr_2O_2	Natural gas, H_2	800-1000 °C
Direct Methanol Fuel Cell (DMFC)	H^+ conducting Membrane	CH_3OH	80-130 °C

The table compares the various types of fuel cells according to the electrolyte, fuel used and the operating temperature. Usually the electrolyte used is dependent on the type of electrochemical reactions involved, the operating temperatures, and the application of the power produced.

Among the various types of fuel cells, the polymer exchange membrane fuel cell (also known as proton exchange membrane fuel cell, PEMFC) is of great interest in this research for reasons such as long life span, low operating temperatures, low weight, compactness, potential for low cost, fast start-ups, suitability to discontinuous operation and sustained operation at high current density.²⁰ The PEMFC usually employs a solid polymer electrolyte for the separation of the fuel from the oxidant. Although the methanol fuel cell (DMFC) is similar to the PEMFC in that it employs the polymer membrane as electrolyte, it produces CO_2 as a byproduct from the methanol used. It also suffers from the high rate of methanol crossover.²⁰

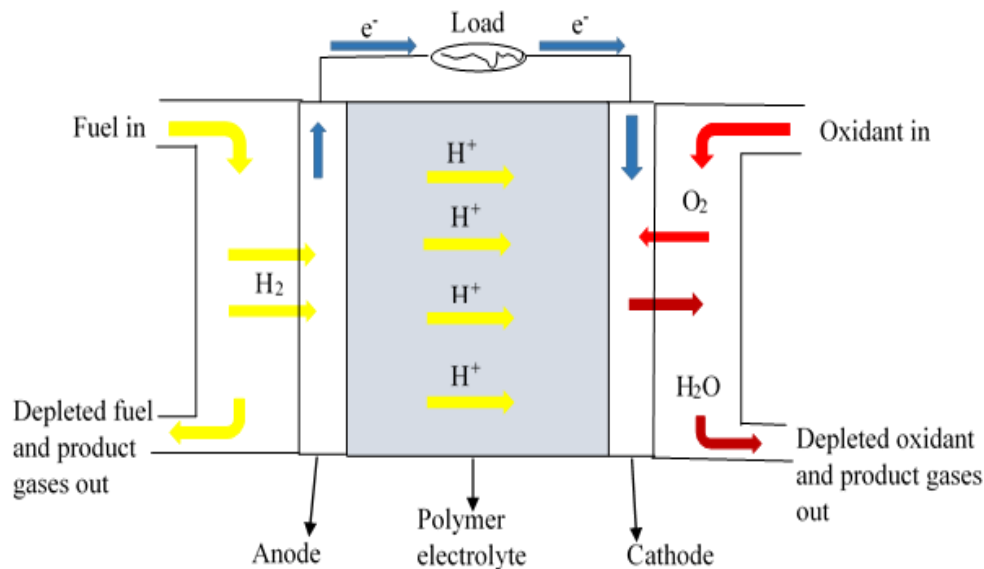
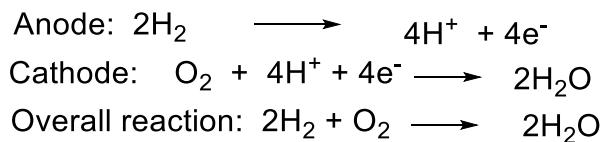


Figure 2: The structure of the PEM fuel cell (modified from Thampan).²³

The electrochemical reaction (Scheme 5) that occurs in the PEMFC includes the oxidation of hydrogen to protons and electrons at the anode in the catalyst layer. As shown in Figure 2, the electrons produced travel along the external circuit to generate electricity. The proton conducting membrane allows the passage of the protons produced to the catalyst layer at the cathode. At the cathode, the protons and electrons chemically combine with the reduced oxygen from air to produce water. The proton conducting membrane does not allow the passage of electrons because it is not electrically conducting. In the PEMFC, the reactions are shown as below:



Scheme 5: The reactions occurring in a PEM fuel cell.

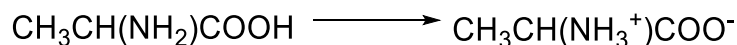
For PEMFC, one of the best known and widely used membranes is the perfluorinated sulfonic acid (PFSA) polymers, such as Nafion[®], due to their good chemical and mechanical

stability at low temperatures.²⁴ However, there are some limitations for PFSA polymers, such as decreased proton conductivity at higher temperatures, short life span due to the gradual loss of electrolyte activity, relatively weak electrode-electrolyte bonding, and poor water management.²⁵

Diazonium PFSI Zwitterionic Monomers

In past years, PFSI polymers were proposed to replace the PFSA polymers for the electrolyte in PEMFC.²⁶ The PFSI polymers are well known to have greater thermal stability in the acid form, inertness to electrochemical conditions, and lower susceptibility to oxidative degradation and dehydration compared to PFSA polymers.²⁶ The zwitterionic monomers is expected to polymerized before or after grafted onto the carbon electrode.

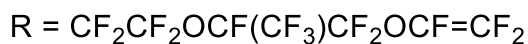
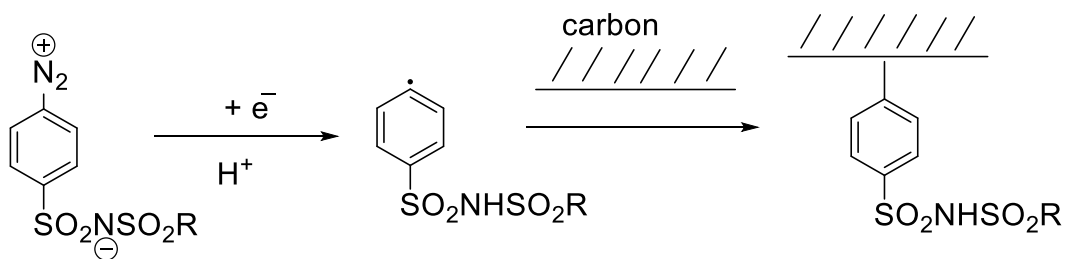
These PFSI zwitterionic monomers are comparable more stable than regular diazonium compounds. The first reason is that they are zwitterions. Zwitterions are the salts that possesses substituent groups with the anion and cation contained in the same molecule. A traditional example of zwitterions is an amino acid containing an ammonium and a carboxylate group at the iso-electric point. Furthermore, zwitterions are described as semipolar compounds because they have significant charge separation between the directly bonded atoms. In semipolar groups, a filled orbital on one atom and an unfilled orbital on the other are inductively distorted by the charge separation.²⁷ The second reason is that the monomers are quite large with the PFSI pendant. Small diazonium compounds are generally known as explosive.



Scheme 6: An example of an amino acid zwitterion.

Furthermore, the diazonium compounds are expected to be attached to the carbon electrode by covalent carbon-carbon bonds, thereby achieving a better intimate integration between the electrolyte and the electrodes for PEM fuel cells. As shown in Scheme 6, the carbon

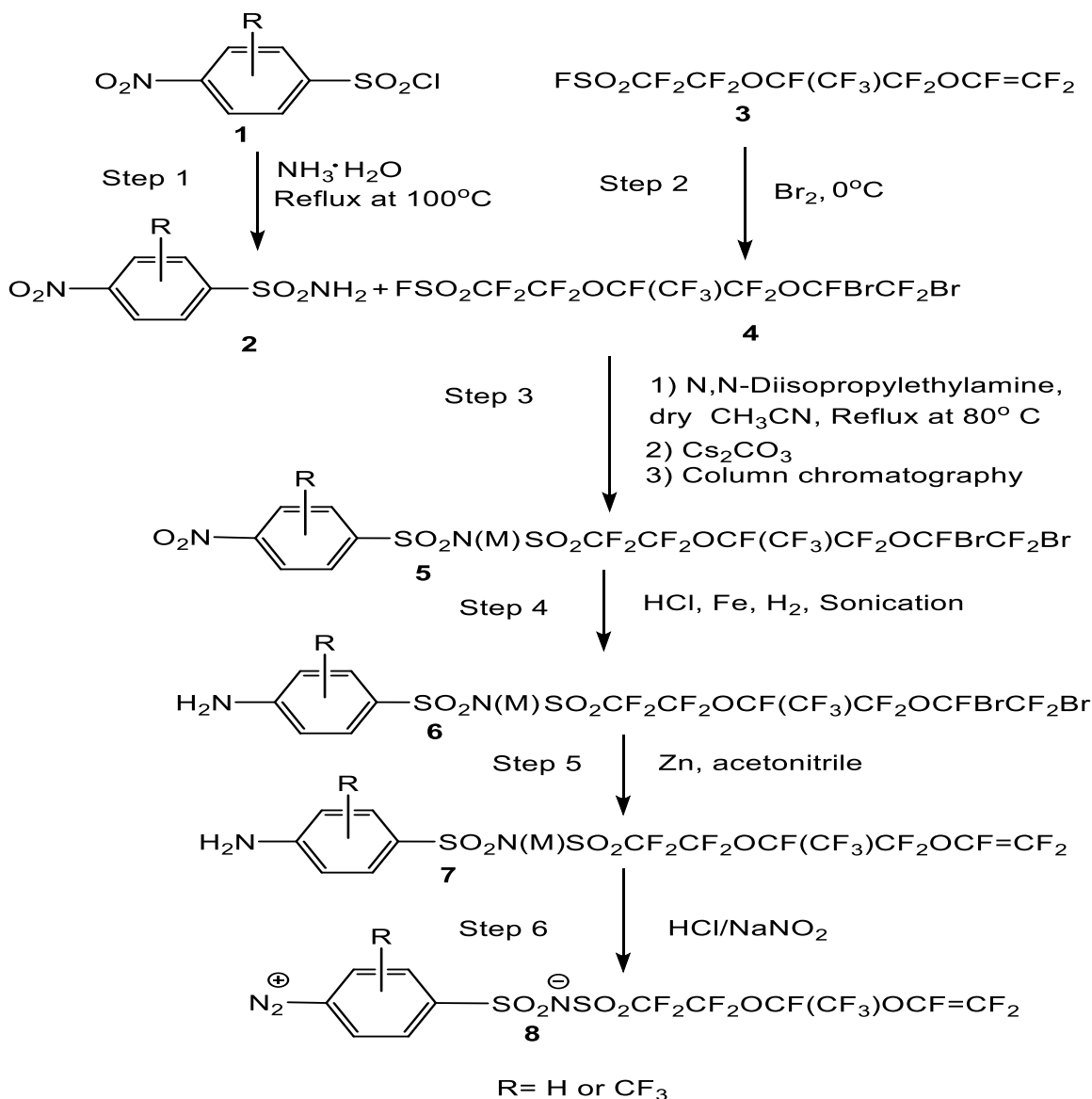
support is expected to be modified with a functional diazonium zwitterion by losing the diazonium group $-N_2^+$ via thermo or reductive electro-chemical reaction.²⁸



Scheme 7: The grafting of the FDZ on the carbon electrode (FDZ is a functional diazonium zwitterion).

Finally, the PFSI monomers can also be copolymerized with tetrafluorovinyl ether to provide excellent thermal and mechanical stability as electrolytes.³⁰ Therefore the synthesis of these diazonium PFSI zwitterionic monomers is very crucial for PEM fuel cell technology.

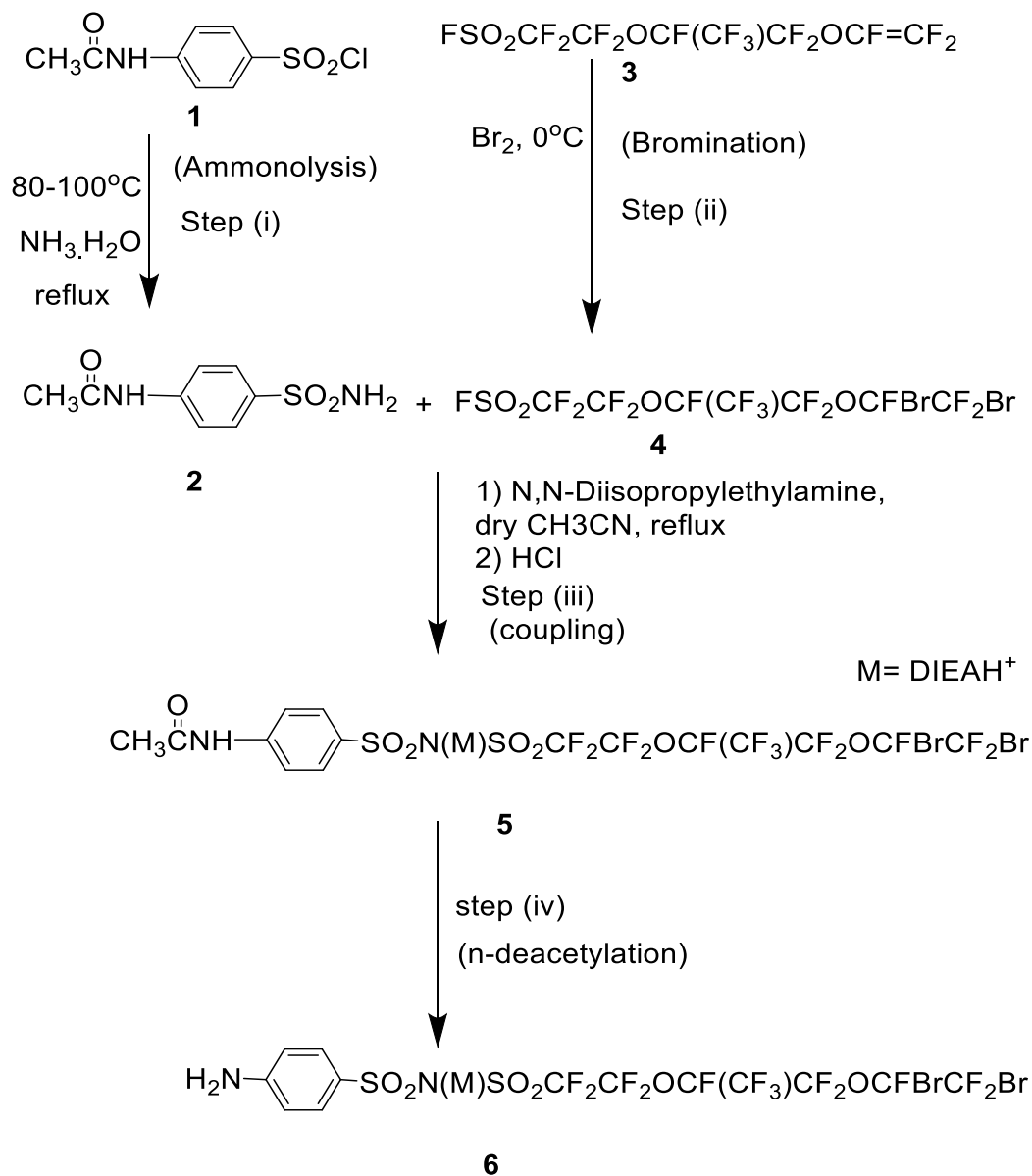
Recently, two forms of these diazonium PFSI monomers have been synthesized. The synthesis is shown in Scheme 8. The synthesis of these diazonium PFSI monomers involves the use of Fe/HCl/H₂ gas to reduce the nitroaromatics to aminoaromatics (Step 4 in Scheme 8) which can further be converted to the diazonium. But it is problematic to completely remove the inorganic impurity, such as an iron chloride complex, from the aminoaromatics after reduction.²⁹



Scheme 8: The previously published overall synthesis scheme.^{29, 30}

To improve the previously published synthetic design, acetamide aromatics are used instead of the nitro aromatics. This is expected to provide the corresponding aminoaromatics, which are the precursor for diazonium salt formation. This research therefore aims at studying various methods for *N*-deacetylation of the PFSI aromatic acetamide (**5** \rightarrow **6** in **Scheme 9**). The use of acetamide is expected to expedite both the ammonolysis and coupling reactions due to the high nucleophilicity of acetamide based aromatics compared to the nitroaromatics in a typical

SN₂ reaction. This method is expected to provide the aminoaromatics with better yield and purity due to the absence of inorganic impurities such as iron chloride complex which is associated with the previous synthetic design.



Scheme 9: The proposed synthesis scheme.

The *N*-deacetylation is designed to be completed before debromination to prevent any possible electrophilic or nucleophilic reaction toward the perfluorinated olefin moiety. The reason is that amide hydrolysis requires harsh reaction conditions, such as a strong acid or base

at high temperature.¹¹ Such harsh reaction conditions limits the *N*-deacetylation in terms of the compatibility of perfluorinated olefins. Methods to remove the acyl group from the amide via general acid under mild conditions were developed in our lab. The purity, reaction time and percentage yields of the new synthetic route were explored and compared.

Since the debromination of vicinal dibromides of PFSI compounds were successfully carried out in our lab with base,²⁹ one pot reaction of *N*-deacetylation and debromination was under investigation with base catalyst to possibly shorten the previously published overall synthetic design for the diazonium PFSI monomers.

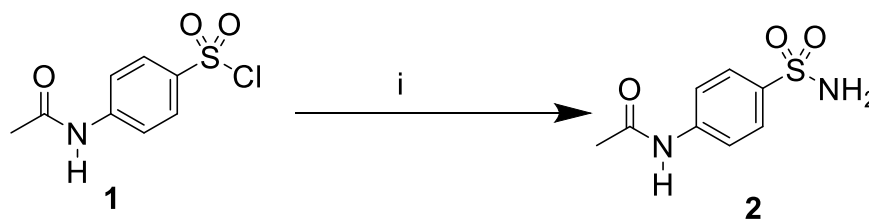
CHAPTER 2

RESEARCH AND DISCUSSION

The main focus of this research was the methodological study of the *N*-deacetylation reaction of 4-acetamido-perfluoroalkylbenzenesulfonimide to provide 4-amino-perfluoroalkylbenzenesulfonimide, which was the fourth step for the synthesis of diazonium PFSI monomers. There were three other steps namely; ammonolysis reaction, bromination reaction and coupling reaction, before the *N*-deacetylation reaction. The synthesized compounds were characterized by ^1H NMR, ^{19}F NMR, GC-MS and IR spectroscopy.

Ammonolysis Reaction of 4-Sulfamonylacetanilide

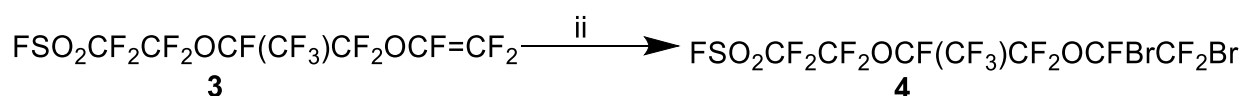
The synthesis of 4-sulfamonylacetanilide **2**, from *N*-acetyl sulfanilyl chloride **1**, was carried out by refluxing it in the presence of excess ammonium hydroxide and acetonitrile. The stoichiometric mole ratio of sulfonyl chloride to aqueous ammonia was 1:2 respectively. This $\text{S}_\text{N}2$ reaction, as shown in Scheme 10, involved the replacement of the Cl^- ion with the NH_2^- group. Next, the unreacted ammonia neutralized the byproduct HCl . The ammonolysis prevailed over the hydrolysis because NH_3 is a better nucleophile than H_2O . The “sulfonic acid” formed by hydrolysis was converted to the water soluble ammonium salt. Pure 4-sulfamonylacetanilide **2** was isolated by vacuum filtration since both the hydrolysis by-product and side-product NH_4Cl are completely soluble in water. A yield of 74 % was obtained.



Scheme 10: The ammonolysis reaction of *N*-acetyl sulfanilyl chloride (i: Ammonia water 28-30%, reflux at 100 °C overnight).

Bromination of Nafion[®] Monomer

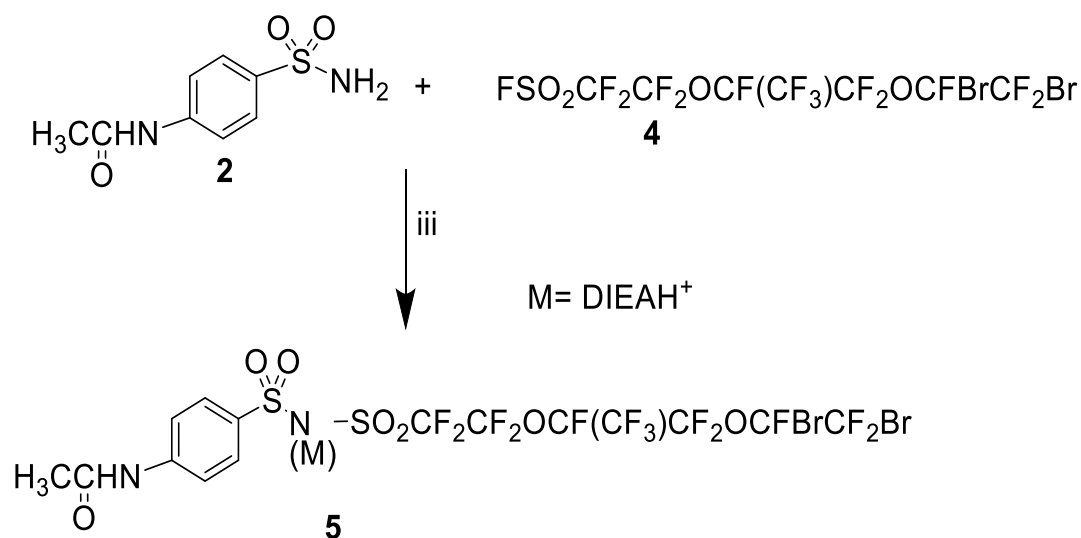
The Nafion[®] monomer **3** was very sensitive to bases at high temperatures because of its strong electron withdrawing perfluoroalkyl group. Hence, it was necessary to protect the double bonds before performing the coupling reaction with base at high temperatures. Protection of the sensitive double bond was achieved through a free radical reaction with bromine liquid at low temperature. Purification of the brominated product **4** was successfully done using vacuum distillation.



Scheme 11: Bromination of Nafion[®] monomer (ii: Br₂, 0 °C to room temperature).

Coupling Reaction

The coupling reaction was done under nitrogen gas protection because the brominated Nafion[®] monomer not only reacts with aryl sulfonyl amide at high temperatures but also can be attacked by weak base catalyzed water to form the hydrolyzed product. The nucleophilicity of the sulfonyl amide –SO₂NH₂ is increased when catalyzed by an organic base such as diisopropyl ethylene amine (DIEA). Compared to the nitro group, the acetamide as a moderate electron donating group, can further boost the rate of the coupling reaction.



Scheme 12: The coupling reaction of 4-sulfamoylacetanilide with Brominated Nafion[®] Monomer (iii: N, N-Diisopropylethylamine, dry CH₃CN, 80 °C for 3 days; Column Chromatography).

The stoichiometric mole ratio for this S_N2 reaction is 1:1.04 of sulfonyl amide **2**, to Nafion[®] monomer **4** respectively. The extra Nafion[®] monomer is used in order to provide enough amounts for the coupling reaction. There are always small amounts of brominated Nafion[®] monomer that will be consumed in the competition hydrolysis reaction. The structure of hydrolysis product **5'** is shown in Figure 3. The hydrolysis product can also be reduced by carrying out the reaction at extremely dry conditions with dry reagents.

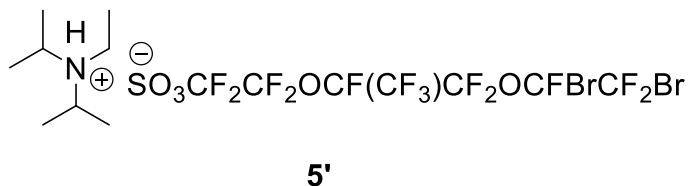


Figure 3: The possible hydrolysis by-product from coupling reaction.

If enough brominated Nafion[®] monomer was not used, or too much hydrolysis consumed the monomer, the sulfonamide will be left out as an impurity as well. Hence column

chromatography was run to remove the extra starting materials sulfonamide. Also the crude coupling product was sticky due to its DIEAH⁺ counter ion. The DIEAH⁺ segment was then converted to acid and removed by solvent extraction. Surprisingly, *N*-deacetylation occurred at room temperature during the acidification process. It led to further investigation into the *N*-deacetylation of the coupled product **5** under mild conditions.

N-deacetylation of the Coupling Product

N-deacetylation, also called an amide hydrolysis reaction and a nucleophilic acyl substitution reaction, occurs via an addition-elimination mechanism. Due to the less reactivity of amides, the hydrolysis usually will be achieved using strong acids or strong bases at high temperatures according to the literature.^{4, 31} The unexpected *N*-deacetylation of PFSI aromatic acetamide during acidification of the sticky coupling product offers us the opportunity to study such reactions under mild conditions. Therefore, various reaction conditions were designed and explored for the *N*-deacetylation of the coupling product. The reaction conditions are tabulated as follows in Table 2:

Table 2: Results for *N*-deacetylation of the Coupling Product.

Entry	<i>N</i> - Acetamide (mmol)	Catalyst Conc. (mol/L)	Solvent	Condition	Time (hrs.)	% Isolated Yield	% <i>N</i> - deacetylation	% debromination
1	0.197	HCl (4.0)	2 mL H ₂ O + 4 mL Acetone	Reflux	24	88.94	100	0
2	0.197	HCl (4.0)	2 mL H ₂ O + 4 mL Acetone	Sonication	6	91.65	87.33	0
3	0.197	HCl (4.0)	2 mL H ₂ O + 4 mL Acetone	Room temperature	144	83.52	100	0
4	0.197	HCl (3.0)	3 mL H ₂ O + 4 mL Acetone	Reflux	48	91.70	0	0
5	0.197	CH ₃ COOH (7.0)	6 mL H ₂ O + 4 mL Acetone	Sonication	48	81.92	0	0
6	0.197	CH ₃ COOH (7.0)	6 mL H ₂ O + 4 mL Acetone	Reflux	48	82.80	0	0

Table 2 (continued)

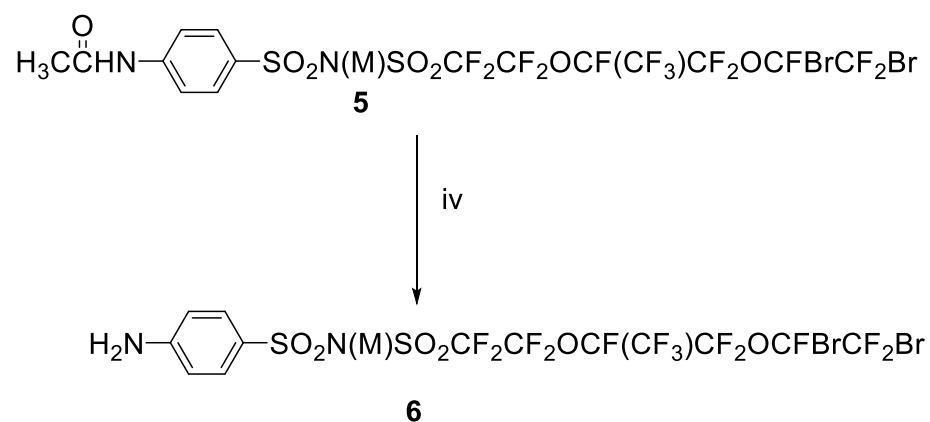
7	0.197	CH ₃ COOH (7.0)	6 mL H ₂ O + 4 mL Acetone	Room temperature	144	84.10	0	0
8	0.197	HCl (4.0)	2 mL H ₂ O + 4 mL Methanol	Reflux	6	84.18	100	0
9	0.197	HCl (4.0)	2 mL H ₂ O + 4 mL Methanol	Room temperature	96	82.91	100	0
10	0.197	HCl (4.0)	2 mL H ₂ O + 4 mL Methanol	Sonication	6	83.11	100	0
11	0.197	H ₂ SO ₄ (2.0)	2 mL H ₂ O + 4 mL Methanol	Sonication	6	83.21	100	0
12	0.197	ClSO ₃ H (2.0)	2 mL H ₂ O + 4 mL Methanol	Sonication	6	83.25	100	0
13	0.197	Na ₂ CO ₃ (0.14)	6 mL H ₂ O + 5 mL Acetone	Sonication	6	81.78	0	100

Table 2 (continued)

14	0.197	NaOH (0.14)	6 mL H ₂ O + 5 mL Acetone	Sonication	6	82.33	0	100
15	0.197	Na ₂ CO ₃ (0.14)	6 mL H ₂ O +5 mL Methanol	Sonication	6	82.18	0	100
16	0.197	NaOH (0.14)	6 mL H ₂ O +5 mL Methanol	Sonication	6	82.33	0	100
17	0.197	NaOH (0.55)	6 mL H ₂ O +5 mL Methanol	Sonication	12	82.11	0	100
18	0.197	KOH (0.14)	6 mL H ₂ O +5 mL Methanol	Sonication	6	83.16	0	100
19	0.197	KOH (0.55)	6 mL H ₂ O +5 mL Methanol	Sonication	6	83.10	0	100
20	0.197	Pyridine (5.5)	6 mL H ₂ O +5 mL Methanol	Sonication	6	82.85	0	0

Table 2 (continued)

21	0.197	NaOH (1.64)	6 mL H ₂ O +5 mL Methanol	Sonication	0.5	83.25	0	0
22	0.197	NaOH (3.27)	6 mL H ₂ O +5 mL Methanol	Sonication	0.5	83.28	100	0
23	0.197	NaOH (6.55)	6 mL H ₂ O +5 mL Methanol	Sonication	0.5	83.12	100	0



M=DIEAH⁺

Scheme 13: The *N*-deacetylation reaction of the coupling product. (step iv).

In summary, *N*-deacetylation of the coupling product was effective under acidic media such as high concentrations of HCl (entries 8, 10 in Table 2) sonication or refluxing. Compared to entry 4 in Table 2, it is clearly indicating that the concentrated HCl was required for this transformation. It may be due to the C-N bond easier to break after the nitrogen is protonated with high concentration of acids (Figure 4).

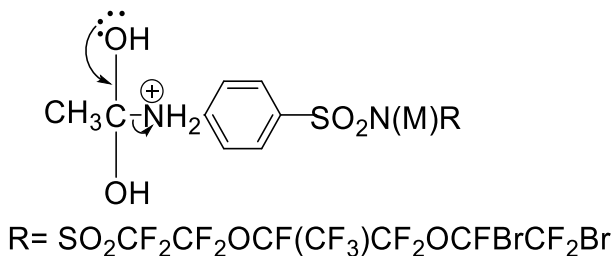


Figure 4: The structure of the protonated amide tetrahedral adduct.

N-deacetylation was also accomplished with other stronger acid catalysts, such as H₂SO₄ (pK_a = -9.0) and ClSO₃H (pK_a = -6.6 entries 11, 12 in Table 2) at a lower concentration compared to HCl (pK_a = -6.0). The stronger the acids, compared to HCl, the less concentration is required for such reaction.

However, *N*-deacetylation was not successful in weak acid such as acetic acid (pK_a = 4.76) because it is not strong enough to attack the acetamide (pK_a = 13, entries 5-7 in Table 2).

Furthermore, changing the aprotic solvent for protic solvent for acid catalyzed reactions increased the rate of reaction substantially (entries 8, 10 compared to 1 in Table 2), although the yield was not improved (around 83%-92% for entries 8, 10 compared to 1 in Table 2). This is as a result of the increased acid proton activity in the presence of the polar protic solvent.

The unidentified impurities from the crude *N*-deacetylated product were successfully removed via column chromatography using a 1:1 tert-butyl methyl ether to acetone solution.

N-deacetylation was also successful in the presence of high concentrations of base under sonication for 30 mins (entries 22 and 23 in Table 2) although side reaction of the perfluorovinyl ether occurred.

The reaction, however, did not occur in the presence of low concentrations of base under sonication for six hours. The complete debromination (100% for entries 13-19 in Table 2) did happen. Therefore, neutralization of the *N*-deacetylated product from the acid catalyzed hydrolysis (entries 1-4, 8-12 in Table 2) led to complete debromination of the coupling product which shortened the overall synthesis scheme.

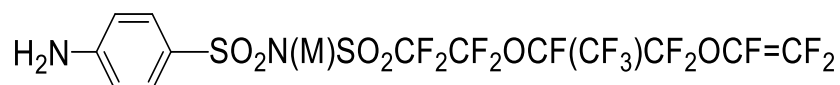


Figure 5: The structure of the debrominated product.

CHAPTER 3
EXPERIMENTAL
General Considerations

NMR Spectroscopy

The ^1H and ^{19}F NMR spectroscopic studies were carried on a Joel JNM-ECP 400 MHz FT-IR spectrometer. The chemical shifts are quoted in parts per million (ppm) using the high-frequency position conversion, and the coupling constants are reported as a 'J' value in Hz. ^1H NMR spectra were referenced to trimethyl silane (TMS) while ^{19}F chemical shifts were referenced to a CFCl_3 external standard. The chemical shift of residual H in CD_3CN is 1.97 ppm relative to TMS. Negative and positive chemical shifts represent upfield and downfield respectively.

The splitting patterns of resonance were described as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The NMR spectra were measured with 1-2 mmol/L concentrations of the solutions (unless indicated otherwise) and small amounts of CFCl_3 external reference in an appropriate deuterated solvent for ^{19}F NMR only.

Gas Chromatography-Mass Spectrometer

GC-MS were recorded on a Shimadzu GCMS-QP2010 Plus GC system spectrometer. The samples were prepared by dissolving 10 mg of the solid samples in 1 mL of acetone.

Infra-Red Spectroscopy

The infrared spectra were recorded on the Shimadzu IR Prestige-21 FT-IR spectrometer. The samples were prepared by putting 1 mg of the solid sample on the lens of the spectrometer. The IR spectra were scanned from 4000 cm^{-1} to 450 cm^{-1} and reported in wavenumbers (cm^{-1}) with intensity abbreviations of: vs (very strong), S (strong), m (medium), w (weak), and vw (very weak).

Glass Vacuum System

The glass vacuum line shown in Figure 6 was used for distillation, drying, sublimation, and purging of compounds. This high-vacuum line was equipped with Teflon[®] and consists of two manifolds where one manifold is for the vacuum and the other is for the nitrogen gas.

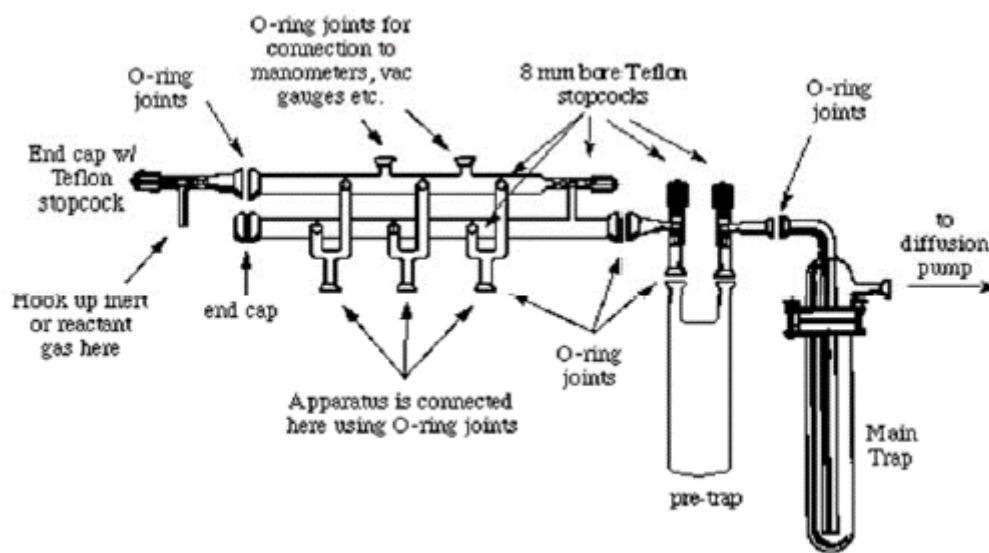


Figure 6: The line diagram of a dual-manifolds glass vacuum line. Used with permission.³²

Thin Layer Chromatography

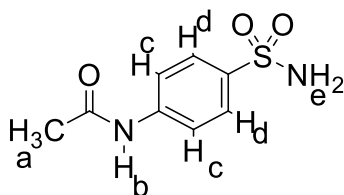
Thin Layer Chromatography (TLC) was conducted with UV active silica gel plates in suitable solvents. The readout was carried out under a UV lamp (254 nm).

Purification of Solvents and Experimental Practice

The starting materials: N-acetyl sulfanilyl chloride and Nafion[®] monomer ($\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}=\text{CF}_2$) were commercially bought from sources and used as received unless otherwise stated. All the reactions were performed in glassware unless otherwise stated. Air or moisture sensitive compounds were stored in a dry box under nitrogen gas. Solvents were dried by transferring them onto activated molecular sieves.

Synthesis of 4-sulfamonylacetanilide

In a typical procedure, *N*-acetyl sulfanilyl chloride (5.01 g, 0.0225 mol) was dissolved in 30 mL of ammonia hydroxide (28-30%) and 20 mL of acetonitrile in a 100 mL round bottomed flask. The solution was refluxed for 24 hrs at 90 °C and the volatile material was removed using a rotary evaporator. The solid crude product was recrystallized from a water-methanol solution and then vacuum filtered. The pure product (3.39 g) of **2** was obtained with a yield of 74.1% after drying under high vacuum for 2 hours.



^1H NMR (400 MHz; CD_3CN ; ppm): δ_a 2.12 (3H, s), δ_b 8.67 (1H, s), δ_c 7.81 (2H, d), δ_d 7.74 (2H, d), $J_{\text{CD}} = 4$ Hz, and δ_e 5.62 (2H, s).

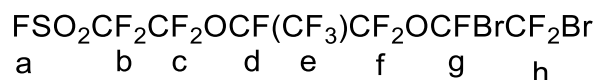
IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3250 m (NH), 1670 m (C=O), 1550 m (NH) and 1300 s (S=O).

m/z : 43 (M^+ , 100%), 214, 172, 156, 108, 92 and 65.

Synthesis of $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$

In a typical procedure, Nafion[®] monomer $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}=\text{CF}_2$ (10.0 g, 22.4 mmol) was added into a 25 mL round bottom flask containing a stir bar. The flask was put in an ice bath at 0 °C. Bromine (2 mL, 39.0 mmol) was added slowly using a pressure equalizing funnel for about 2 hours. Persistence of a reddish color for 30 mins indicated that there was excess bromine. The excess bromine remained in the funnel and as the reaction was allowed to continue overnight in the presence of light, some bromine dissociated and was made available as $\text{Br}_{2(\text{g})}$ encouraging the free radical reaction.

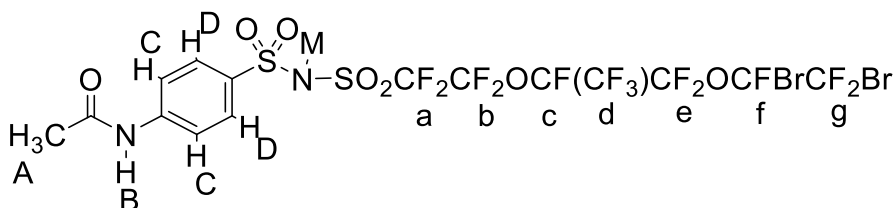
The excess bromine was removed by the addition of 5 % NaHSO₃ slowly until the reddish color disappeared. The product was separated by extraction with 3×5 mL DI water in a separatory funnel. Na₂SO₄ was used to dry the product, after which it was distilled under dynamic high vacuum. A percent yield of 70.5 % (9.56 g) of the product was obtained.



¹⁹F NMR (400 MHz; CD₃CN; ppm): δa 44.24 (1F, s), δb -113.11 (2F, m), δc -80.72 (2F, m), δd -145.90 (1F, m), δe -83.02 (3F, qm), δf -86.50 (2F, AB pattern multiplet), δg -73.75 (1F, m), and δh -66.64 (2F, d).

Synthesis of CH₃CONHPhSO₂N(M)SO₂CF₂CF₂OCF(CF₃)CF₂OCFBrCF₂Br

In a typical procedure, brominated Nafion[®] monomer (3.30 g, 5.44 mmol) and the 4-sulfamonylacetanilide (1.12 g, 5.24 mmol) were added into a 100 mL three-necked round bottom flask equipped with a stir bar and two rubber septa in a dry box. Then 30 mL of acetonitrile and 5 mL of diisopropyl ethylamine (DIEA) were injected into the closed flask subsequently. The solution was refluxed for 3 days at 90 ° C with nitrogen gas protection. ¹⁹F NMR spectroscopy indicated the reaction was complete by the disappearance of the –SO₂F signal. All of the volatile compounds were then removed under vacuum leaving the crude product as the DIEAH⁺ salt and the inorganic impurities. The 1:1 ratio of acetone to tert-butyl methyl ether was used to run through the column to remove the hydrolysis by-product. The final product was filtered and dried under vacuum for 24 hours. The yield was 3.93 g, (81.9 %).



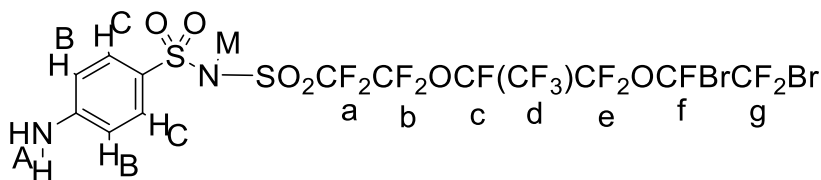
^{19}F NMR (400 MHz; CD_3CN ; ppm): δa -115.41 (2F, m), δb -80.72 (2F, m), δc -144.77 (1F, m), δd -78.63 (3F, qm), δe -85.10 (2F, AB pattern multiplet), δf -71.83 (1F, m), and δg -63.65 (2F, d).

^1H NMR (400 MHz; CD_3CN ; ppm): δA 2.16 (3H, s), δB 9.53 (1H, s), δC 7.85 (2H, d), δD 7.78 (2H, d) and $J_{\text{CD}} = 4$ Hz.

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3400 (NH), 1728.22 m (C=O), 1313.52 m and 1232.51 s (S=O), 1130.29 vs (CF_2).

Synthesis of $\text{NH}_2\text{PhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$

In a typical procedure, the coupled product (0.18 g, 0.197 mmol) was added into a 25 mL round bottom flask equipped with a stir bar. Then 4 mL of methanol and 2 mL of concentrated acid were added to it. The pH of the resulting solution was tested using a pH paper and it was acidic. The solution was allowed to react under the following conditions: reflux or sonication for 6 hours. The solution was then neutralized to pH 7 with NaOH. Next the solvent was removed and the product dried under vacuum overnight. The dried sample was re-dissolved in 4 mL of ethyl acetate, and then transferred into a 65 mL separatory funnel. The organic solution was washed with 3×3 mL of brine water. The solvent was removed and then dried under vacuum. The 1:1 ratio of acetone to tert-butyl methyl ether was used to remove the hydrolysis by-product via column chromatography.



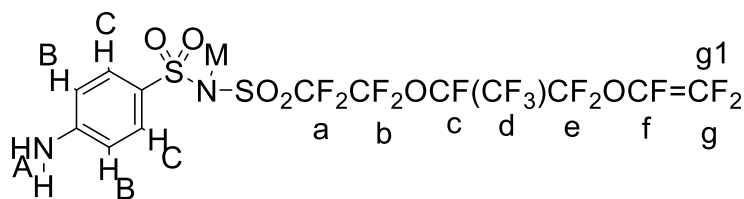
^{19}F NMR (400 MHz; CD_3CN ; ppm): δ_a -115.41 (2F, m), δ_b -80.72 (2F, m), δ_c -144.77 (1F, m), δ_d -78.63 (3F, qm), δ_e -85.10 (2F, AB pattern multiplet), δ_f -71.83 (1F, m), and δ_g -63.65 (2F, d).

^1H NMR (400 MHz; CD_3CN ; ppm): δ_A 4.78 (2H, s), δ_B 7.55 (2H, d), δ_C 6.61 (2H, d) and J_{BC} = 4 Hz.

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3064.89 (NH), 1300 m and 1232.51 s (S=O), 1115 vs (CF_2).

Synthesis of $\text{NH}_2\text{PhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$

In a typical procedure, the coupled product (0.18 g, 0.197 mmol) was added into a 25 mL round bottom flask equipped with a stir bar. Then 5 mL of methanol and 6 mL of base were added to it. The pH of the resulting solution was tested using a pH paper and it was basic. The solution was allowed to react under sonication for 6 hours. Next the solvent was removed and dried under vacuum overnight. The dried sample was re-dissolved in 4 mL of ethyl acetate, and then transferred into a 65 mL separatory funnel. The organic solution was washed with 3×3 mL of brine water. The solvent was then removed and dried under vacuum.



^{19}F NMR (400 MHz; CD_3CN ; ppm): δ_a -115.41 (2F, m), δ_b -80.72 (2F, m), δ_c -144.77 (1F, m), δ_d -78.63 (3F, qm), δ_e -85.10 (2F, AB pattern multiplet), δ_f -112.31 (1F, m), δ_{g1} -135.58 (2F, m) and δ_g -121.31 (2F, m).

^1H NMR (400 MHz; CD_3CN ; ppm): δ_A 4.78 (2H, s), δ_B 7.55 (2H, d), δ_C 6.61 (2H, d) and J_{BC} = 4 Hz.

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3064.89 (NH), 1300 m and 1232.51 s (S=O), 1115 vs (CF_2).

CHAPTER 4

CONCLUSION

An alternative synthetic path has successfully been developed for the synthesis of PFSI diazonium zwitterionic monomers. In this method development, four different compounds were successfully synthesized and characterized. The synthesized compounds obtained are 4-sulfamonylacetanilide, $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$, $\text{CH}_3\text{CONHPhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$ and $\text{NH}_2\text{PhSO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$ from the ammonolysis, bromination, coupling and *N*-deacetylation reactions respectively.

Ammonolysis of 4-sulfamonylacetanilide was achieved by reacting *N*-acetyl sulfanilyl chloride and ammonium hydroxide in a ratio of 1:2 under reflux overnight. Similarly protection of the sensitive double bonds of the Nafion[®] monomer was accomplished in a free radical reaction where the monomer was reacted with bromine liquid at 0 °C overnight. Coupling of 4-sulfamonylacetanilide and the brominated Nafion[®] monomer occurred in the presence of diisopropyl ethyl amine and acetonitrile under reflux for three days. The ratio of 1:1.04 of amide to Nafion[®] monomer was used in order to have enough of the monomer to react with the amide after part of it had hydrolyzed.

The *N*-deacetylation of 4-acetamido-perfluoroalkylbenzenesulfonimide occurred in the presence of strong acid catalysts under reflux and sonication for six hours in methanol. The reaction time was short compared to regular acetamides due to the electron withdrawing perfluoroalkyl group which destabilizes the carbon-nitrogen bond. This optimized condition will help in the study of the scope of structurally different aromatic acetamides for the synthesis of PFSI diazonium zwitterionic monomers due to ease in purification, short reaction time and

relatively high yields. The debromination of the protected perfluoro vinyl ether was perceived to have occurred via neutralization of the *N*-deacetylated product. It will shorten the overall synthesis scheme for PFSI monomers. Furthermore, changing the solvent from an aprotic one to a protic solvent increased the rate of the reaction significantly.

N-deacetylation in the presence of base at high concentrations was successful although side reactions of the perfluorovinyl ether group occurred. Meanwhile, at low concentrations of base the *N*-deacetylation was not successful but debromination happened instead.

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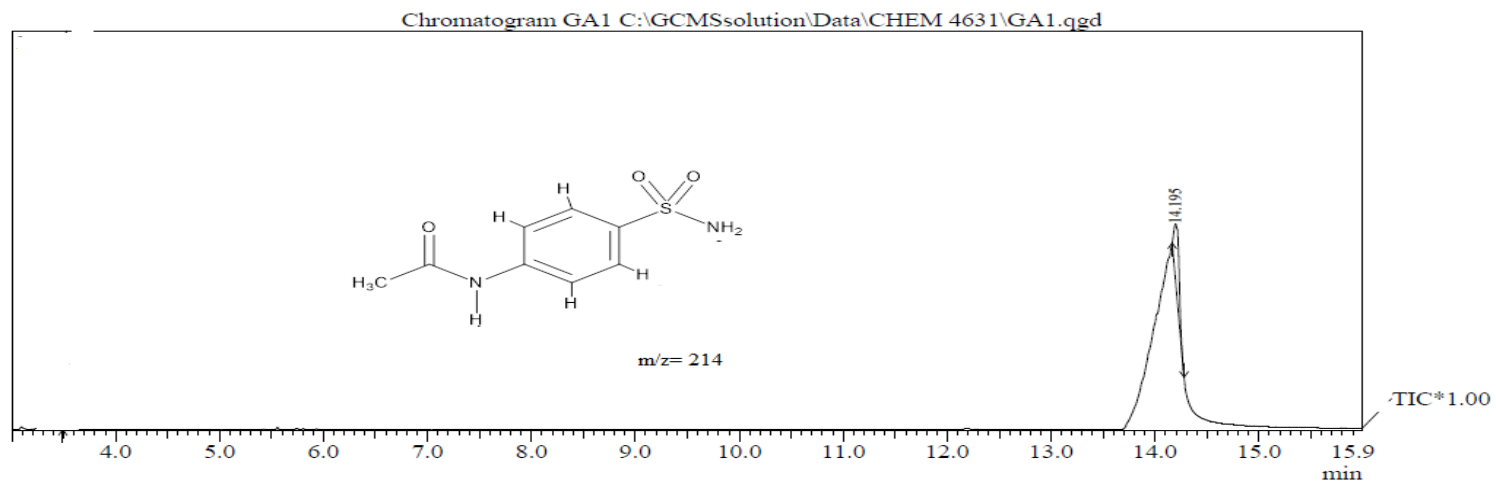
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APPENDICES

APPENDIX A: GC-MS Chromatogram of Compound 2

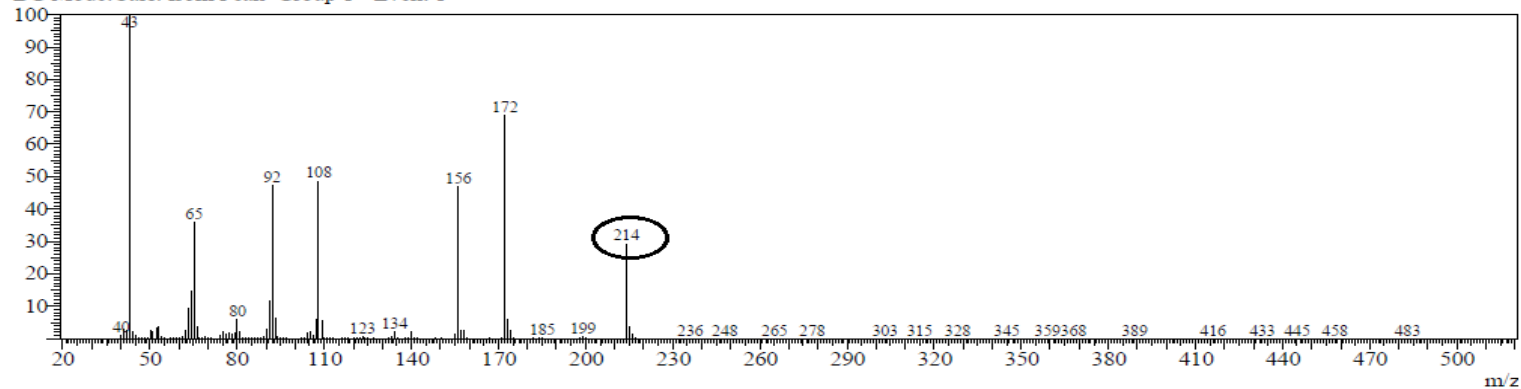


Line#: 2 R.Time: 14.2 (Scan#: 1600)

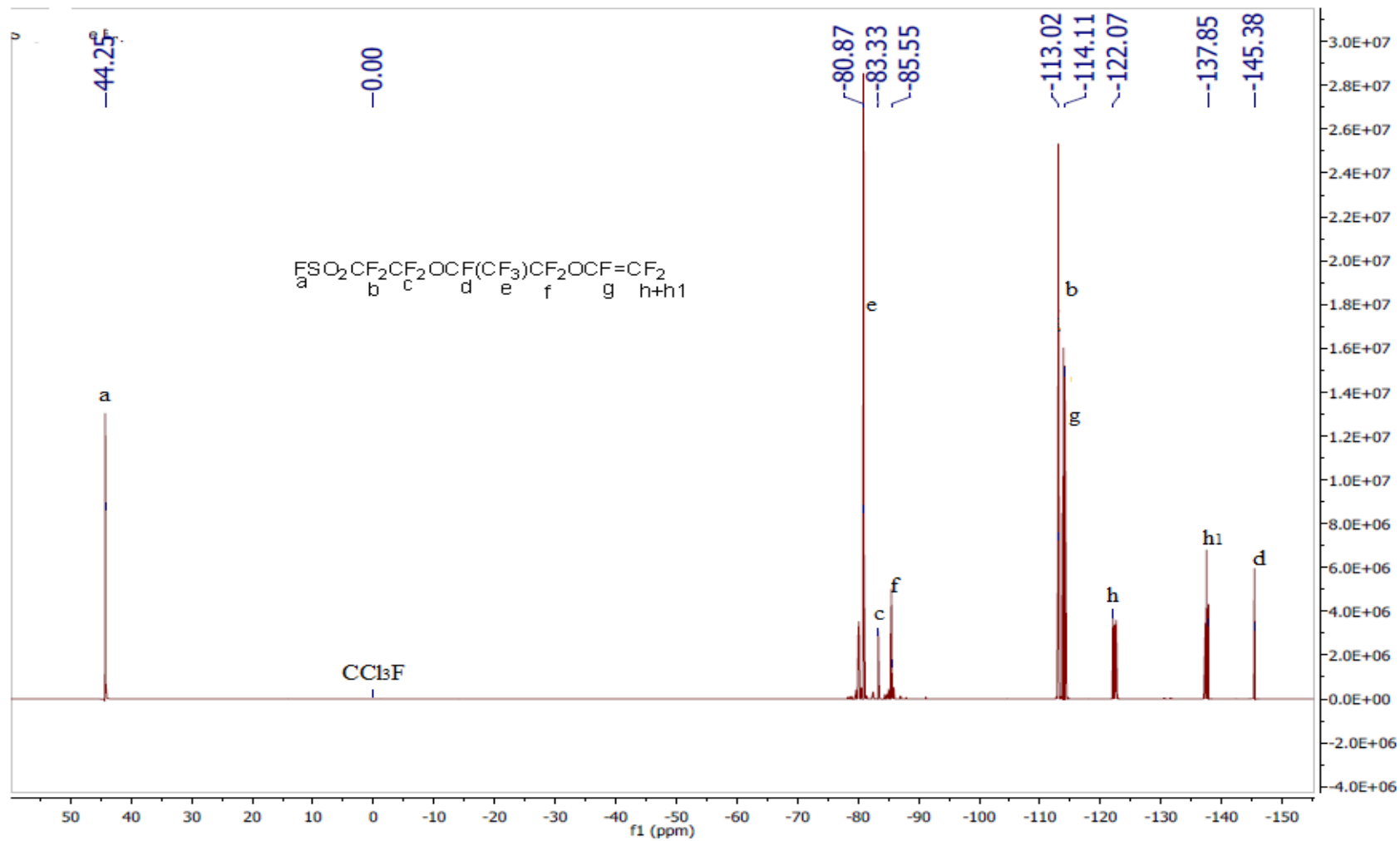
MassPeaks: 284

RawMode: Averaged 14.2-14.2 (1599-1601) BasePeak: 43 (254918)

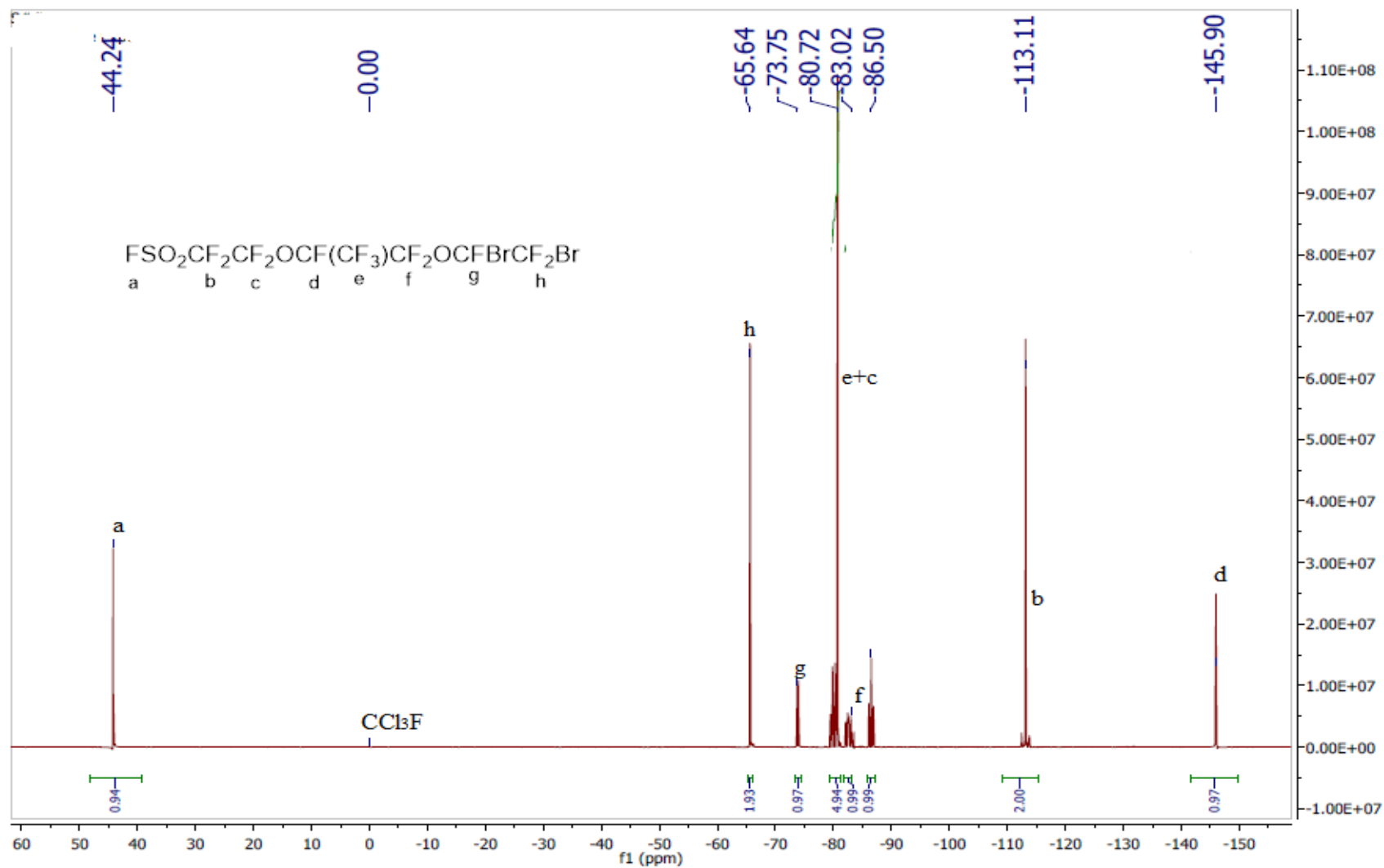
BG Mode: Calc. from Peak Group 1 - Event 1



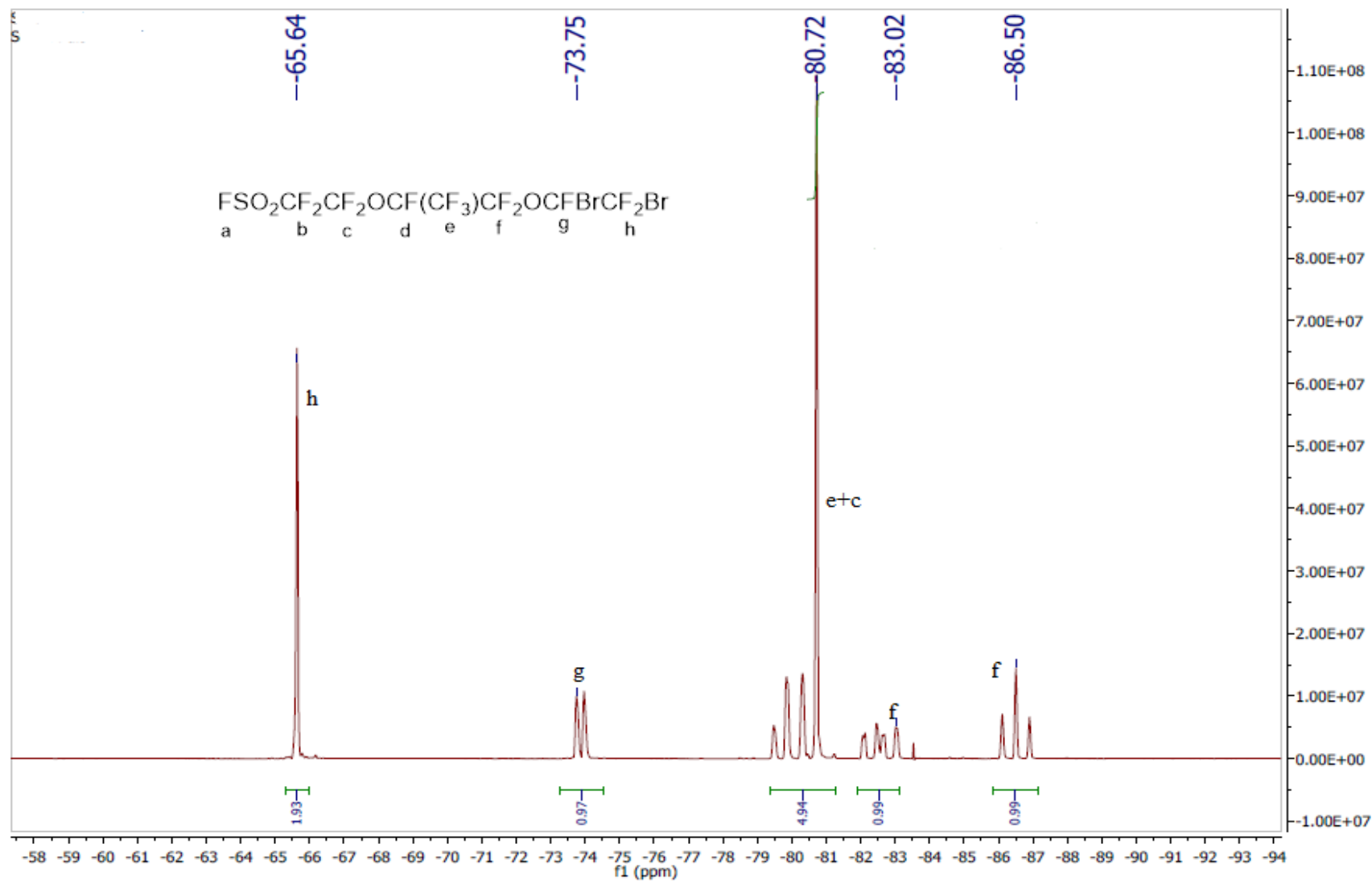
APPENDIX B1: ^{19}F NMR Spectrum of Compound **3**, 400MHz, Acetone- d_6



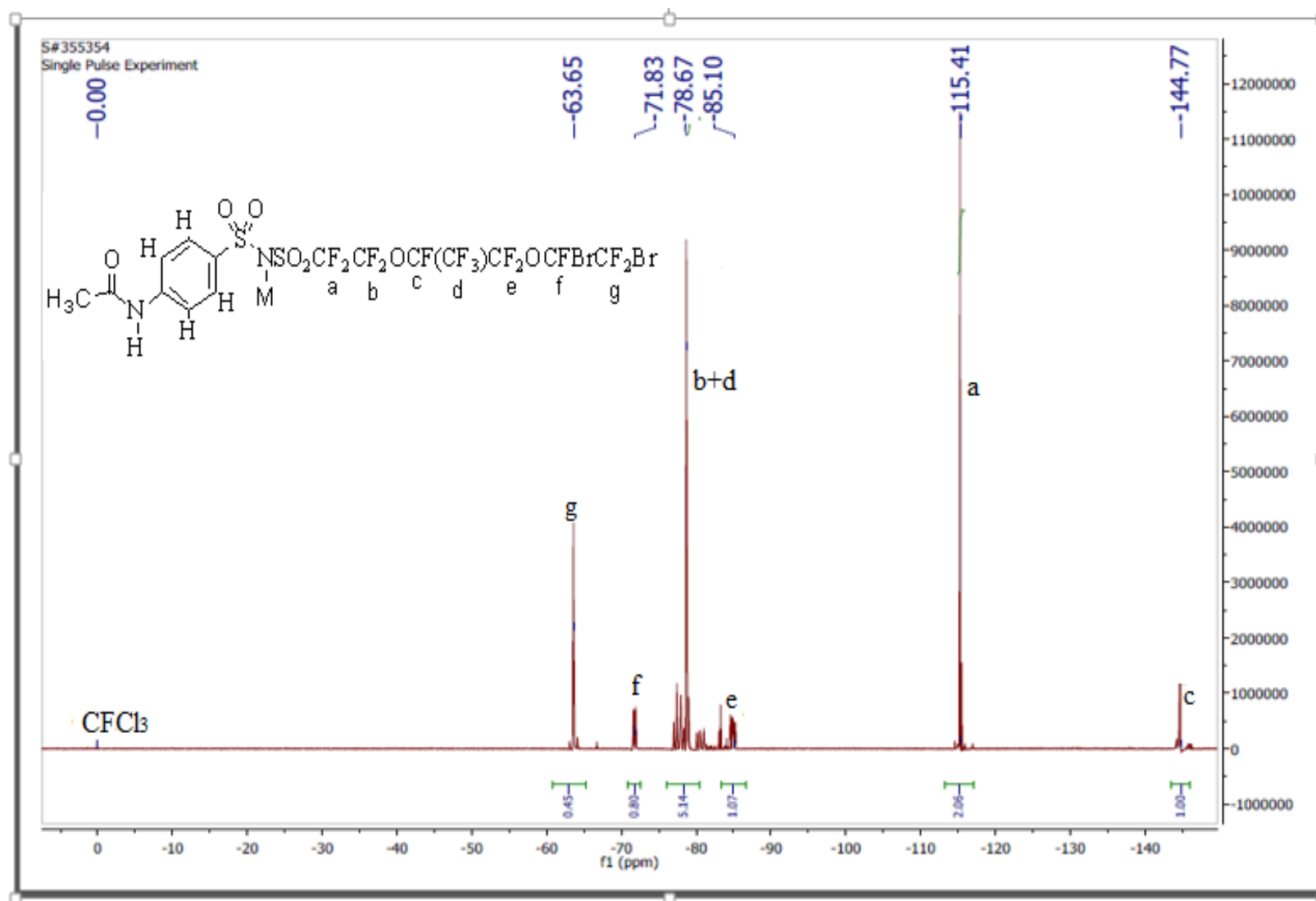
APPENDIX B2: ^{19}F NMR Spectrum of Compound **4**, 400MHz, CD_3CN

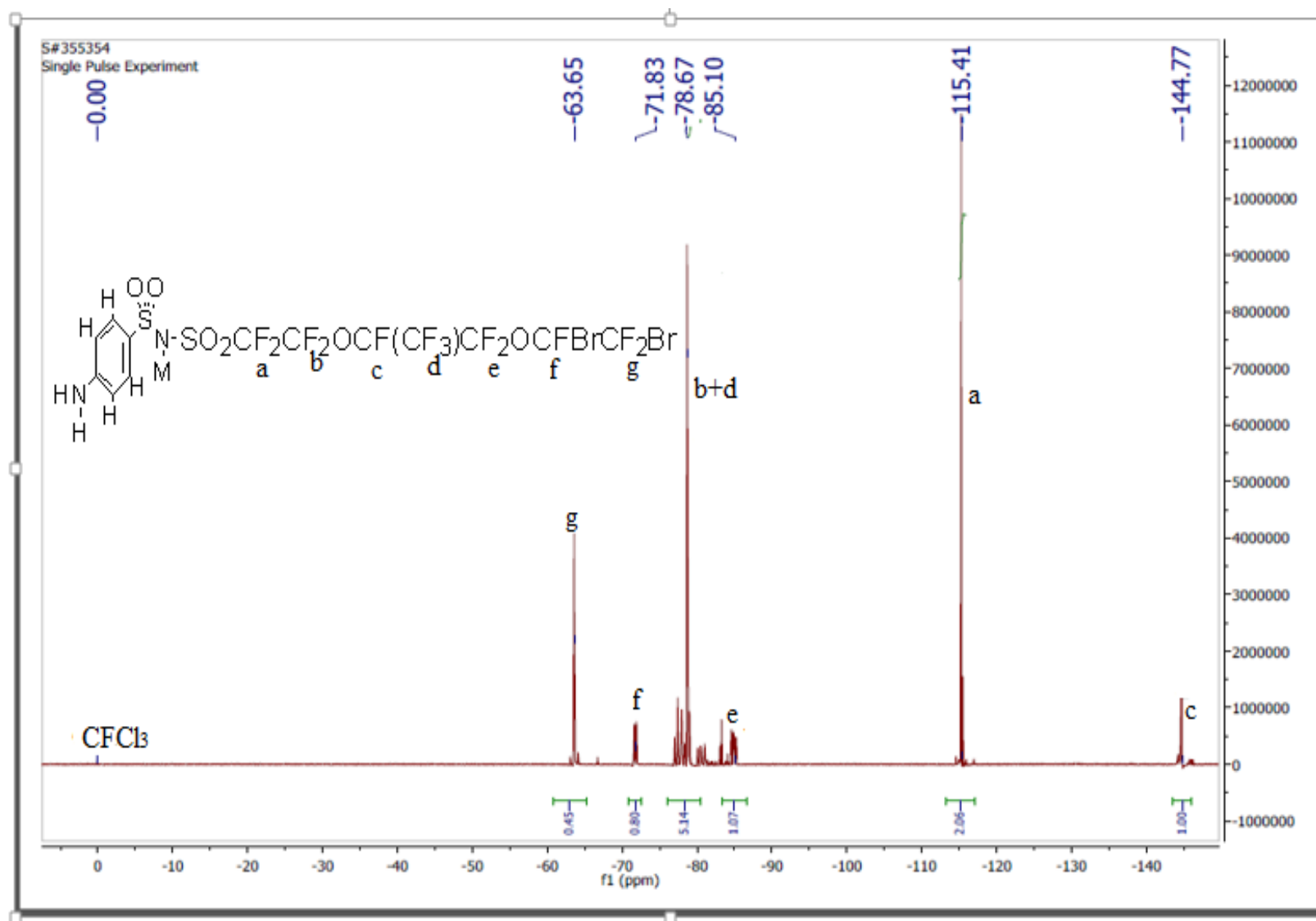


APPENDIX B3: Expanded ^{19}F NMR Spectrum of Compound **4**, 400MHz, CD_3CN

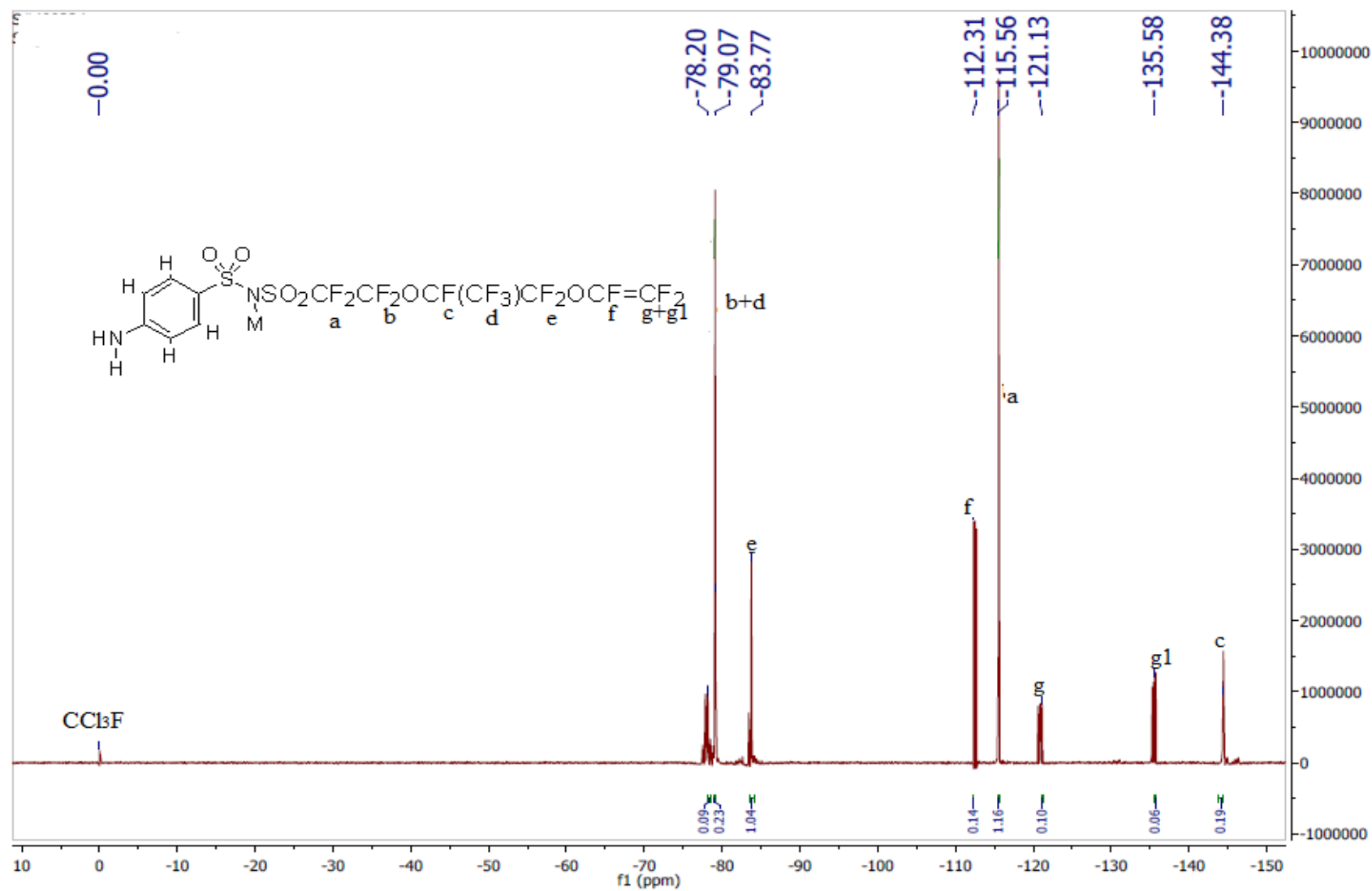


APPENDIX B4: ^{19}F NMR Spectrum of Compound **5**, 400MHz, CD_3CN

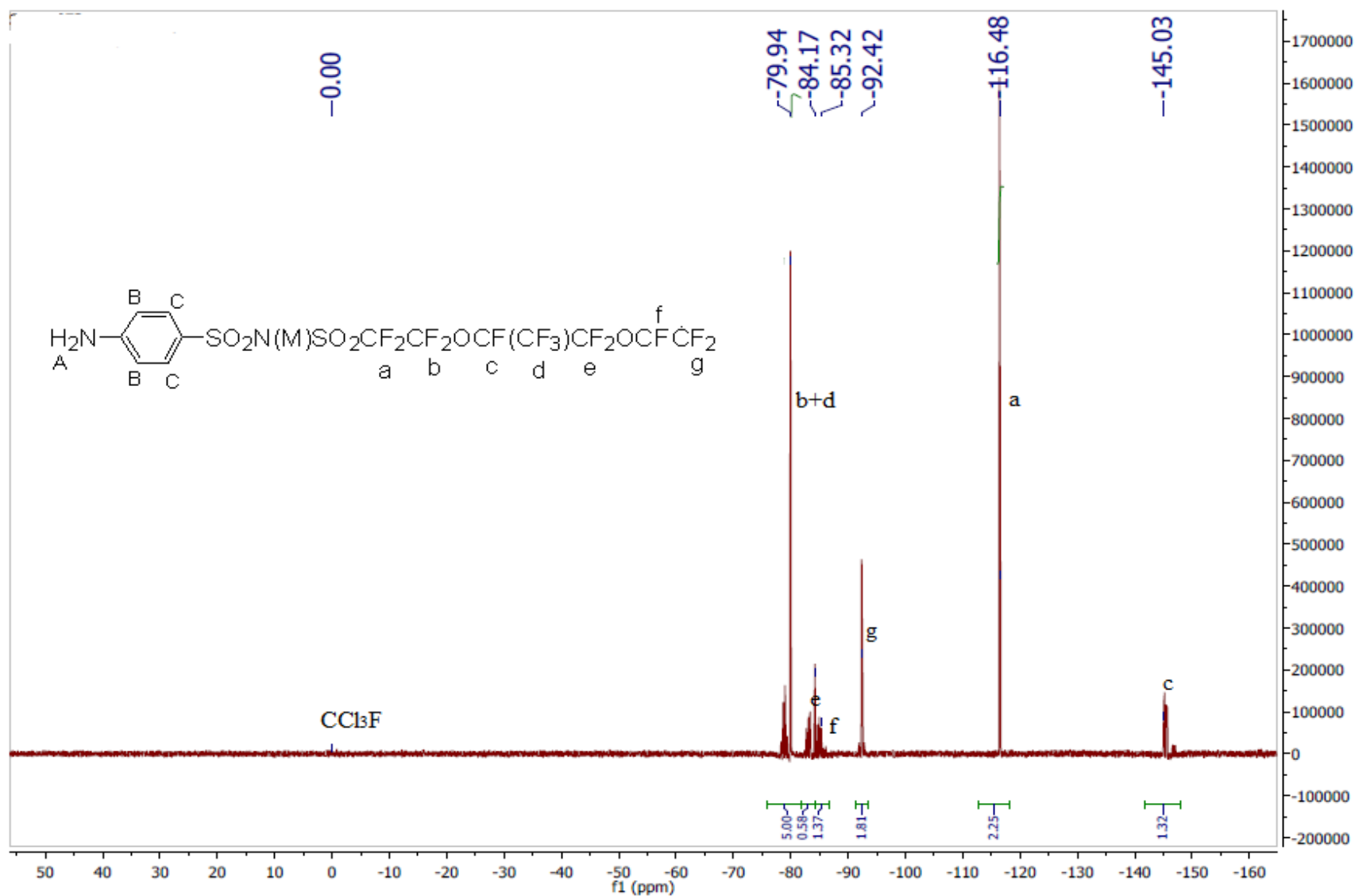


APPENDIX B5: ¹⁹F NMR Spectrum of Compound **6**, 400MHz, CD₃CN

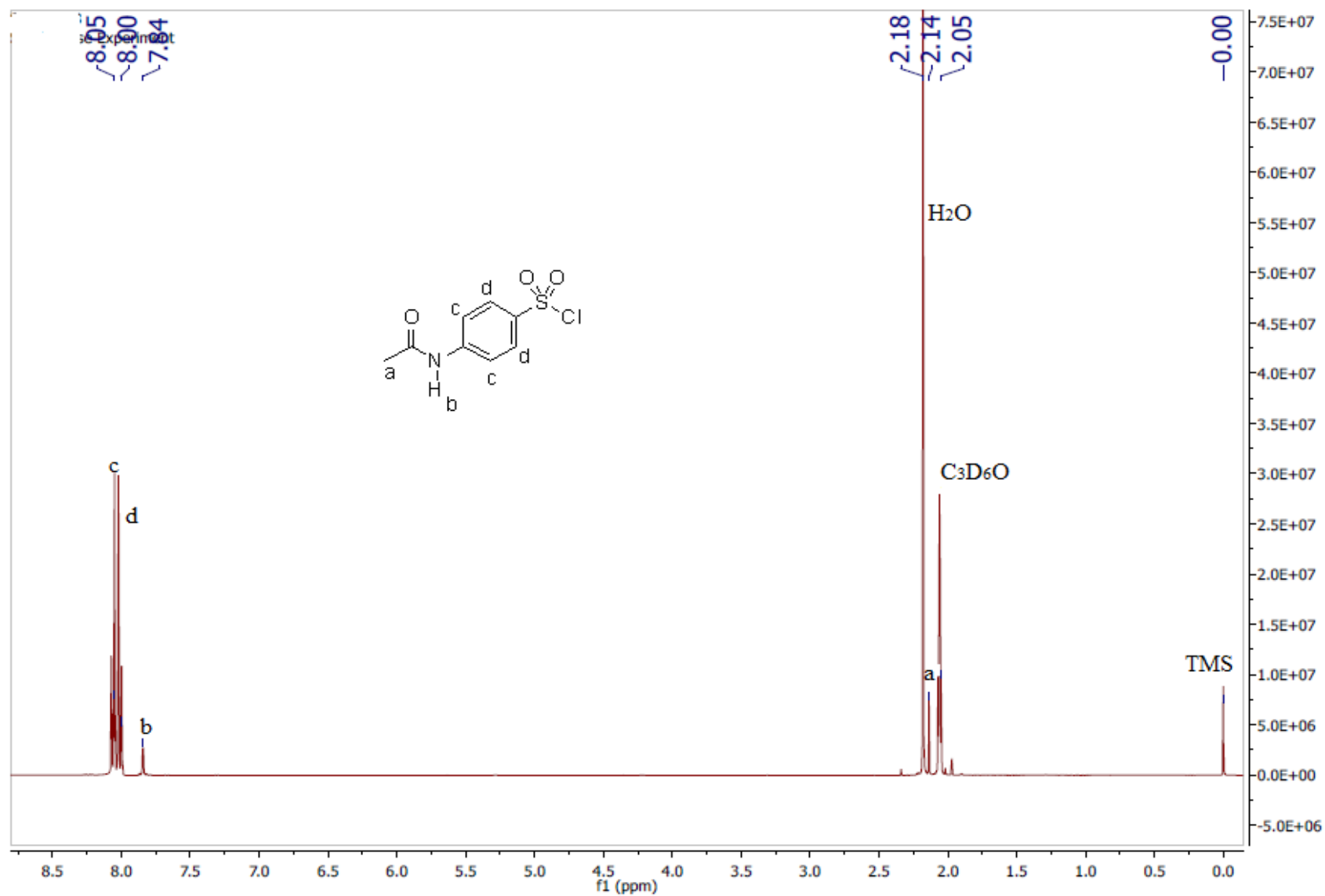
APPENDIX B6: ^{19}F NMR Spectrum of Compound **6'**, 400MHz, CD_3CN



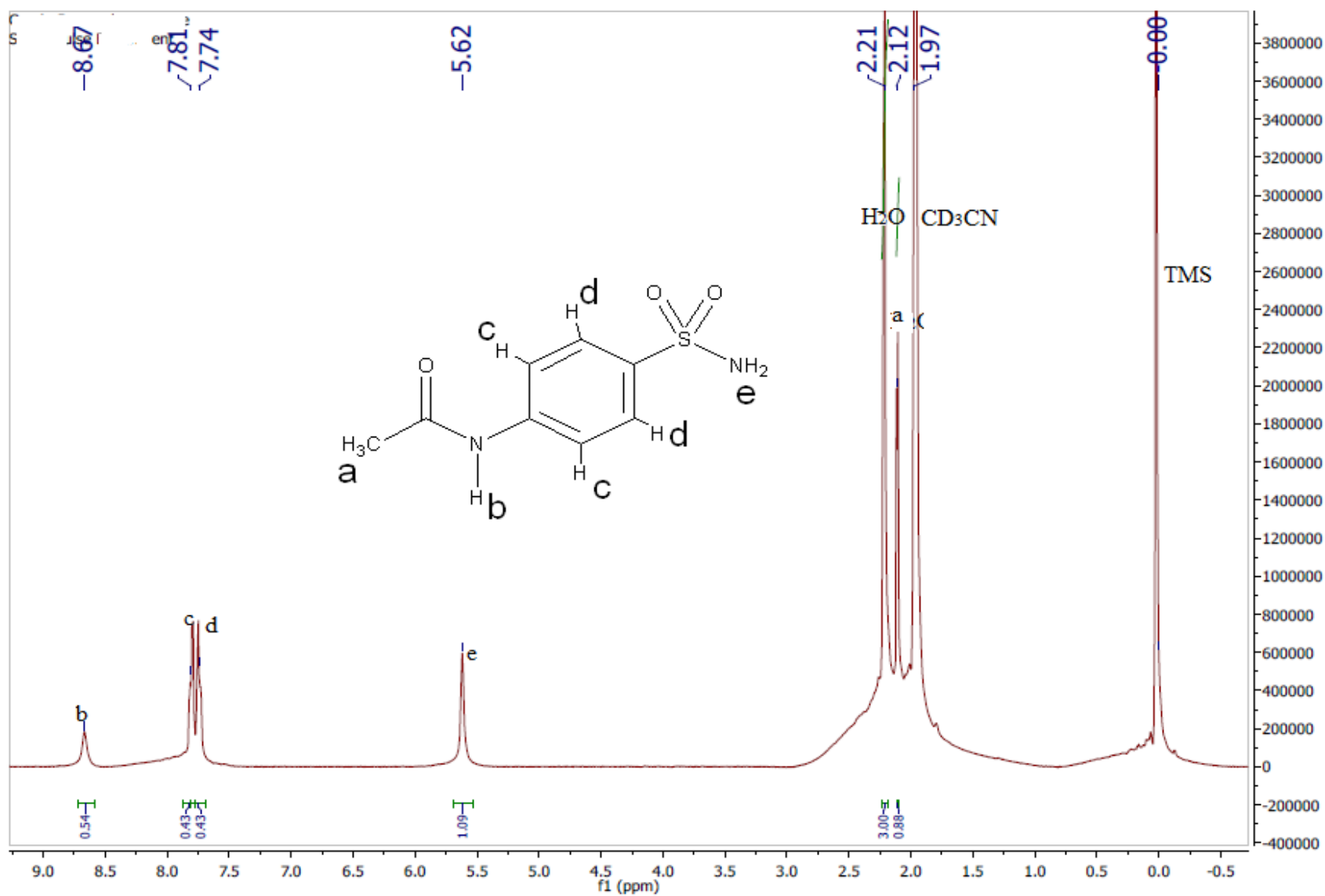
APPENDIX B7: ^{19}F NMR Spectrum of Basic Hydrolysis Byproduct, 400MHz, CD_3CN



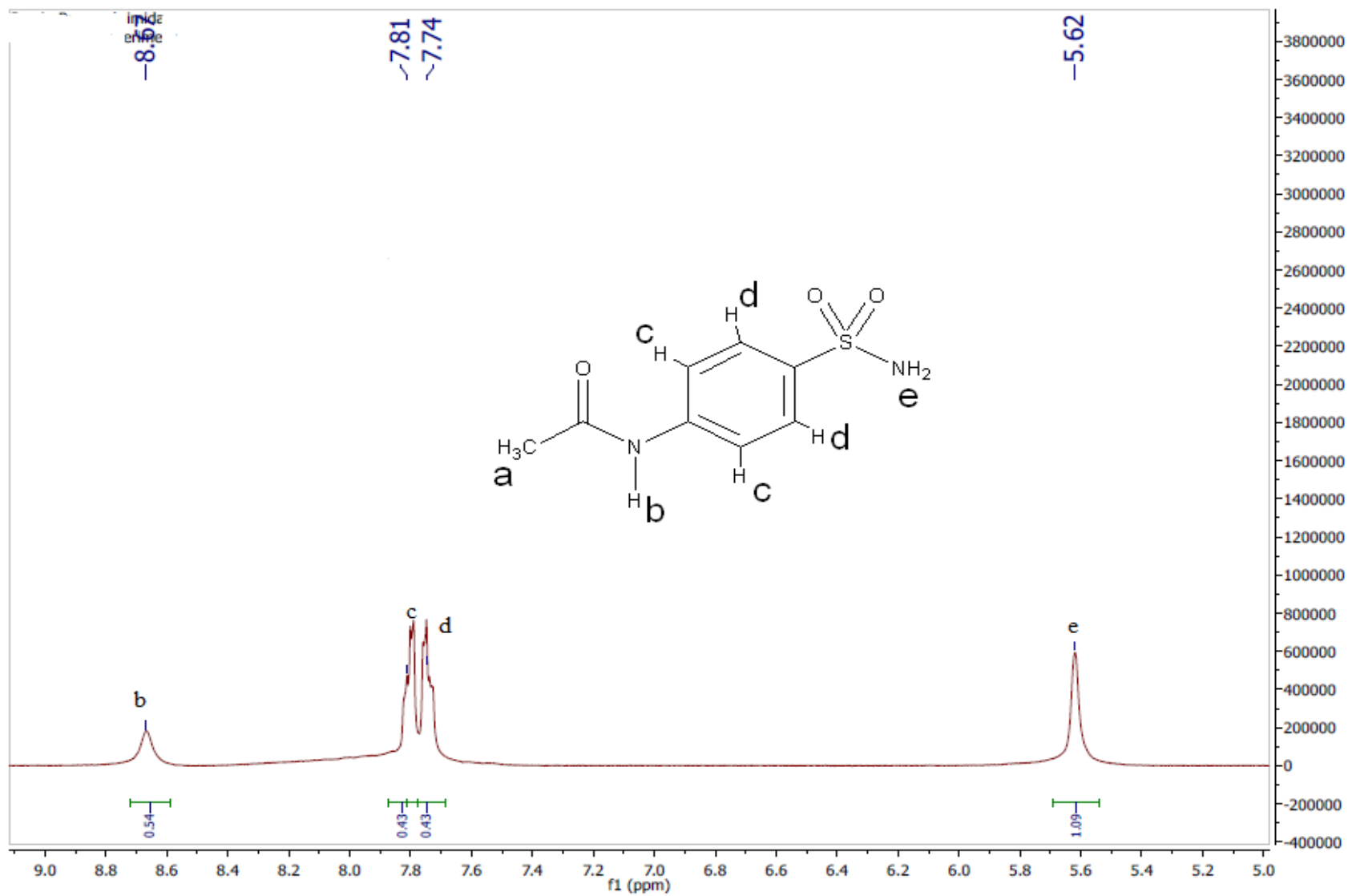
APPENDIX C1: ^1H NMR Spectrum of Compound **1**, 400MHz, Acetone- d_6



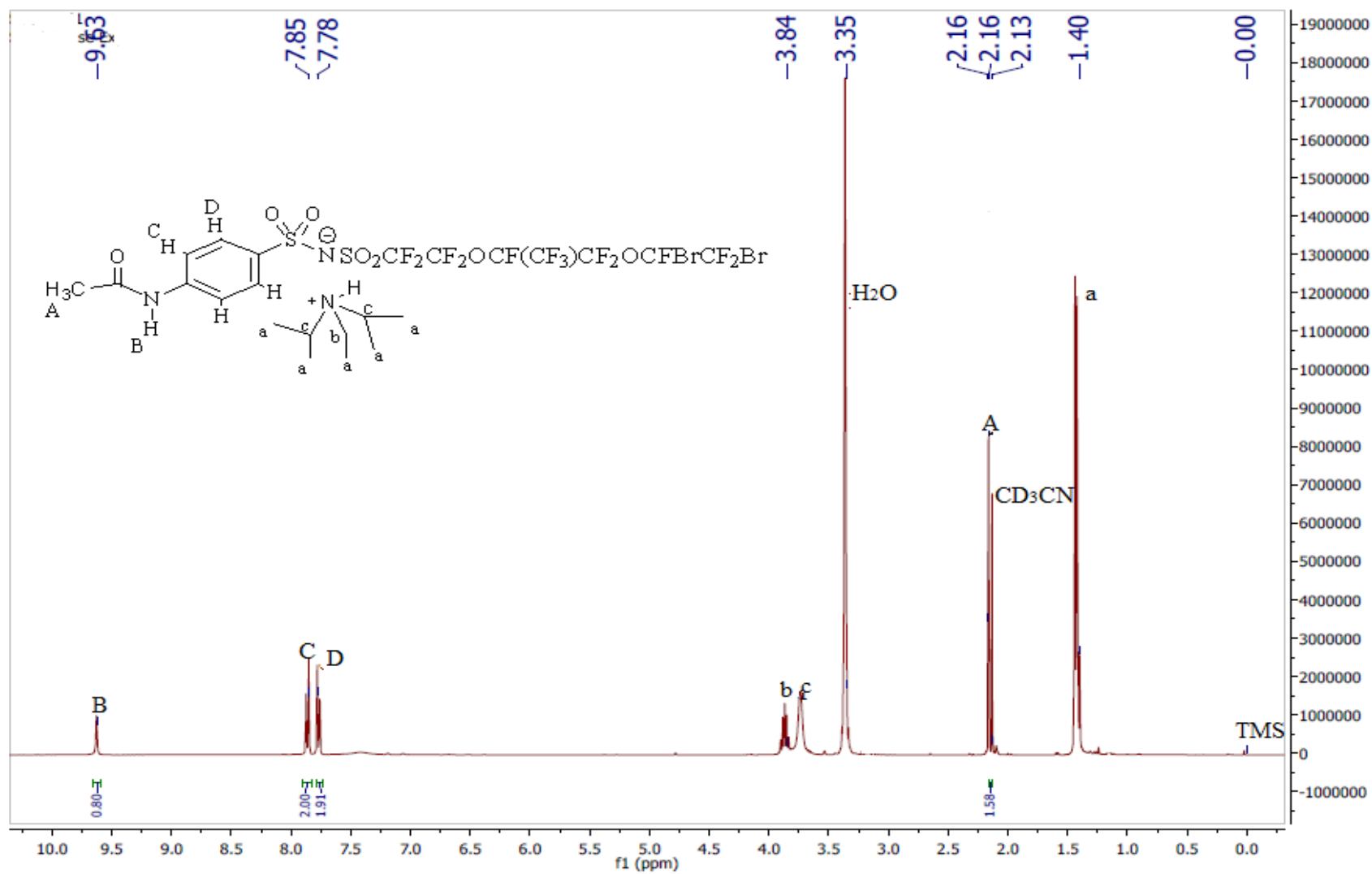
APPENDIX C2: ^1H NMR Spectrum of Compound 2, 400MHz, CD_3CN



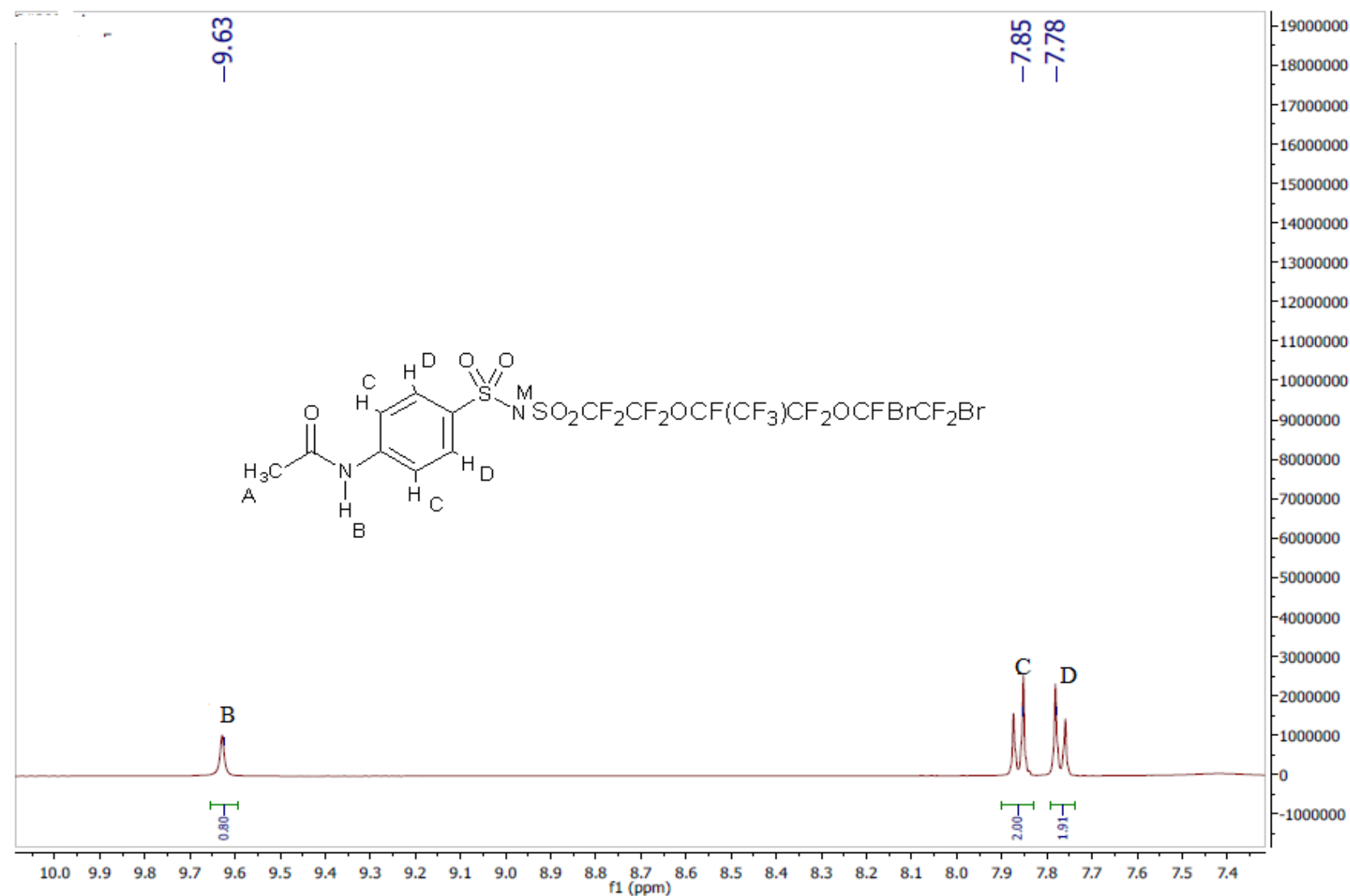
APPENDIX C3: Expanded ^1H NMR Spectrum of Compound **2**, 400MHz, CD_3CN



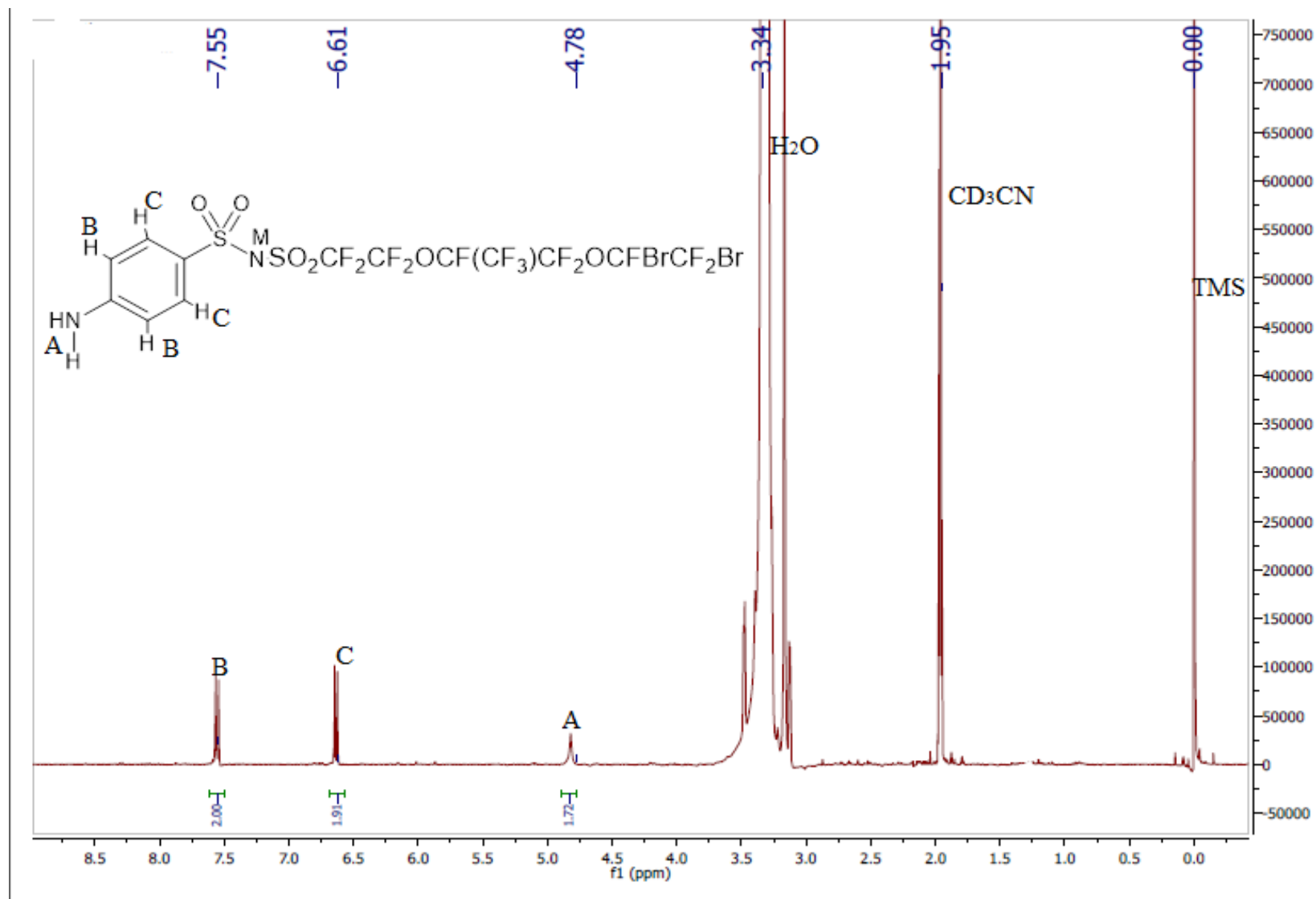
APPENDIX C4: ^1H NMR Spectrum of Compound **5**, 400MHz, CD_3CN



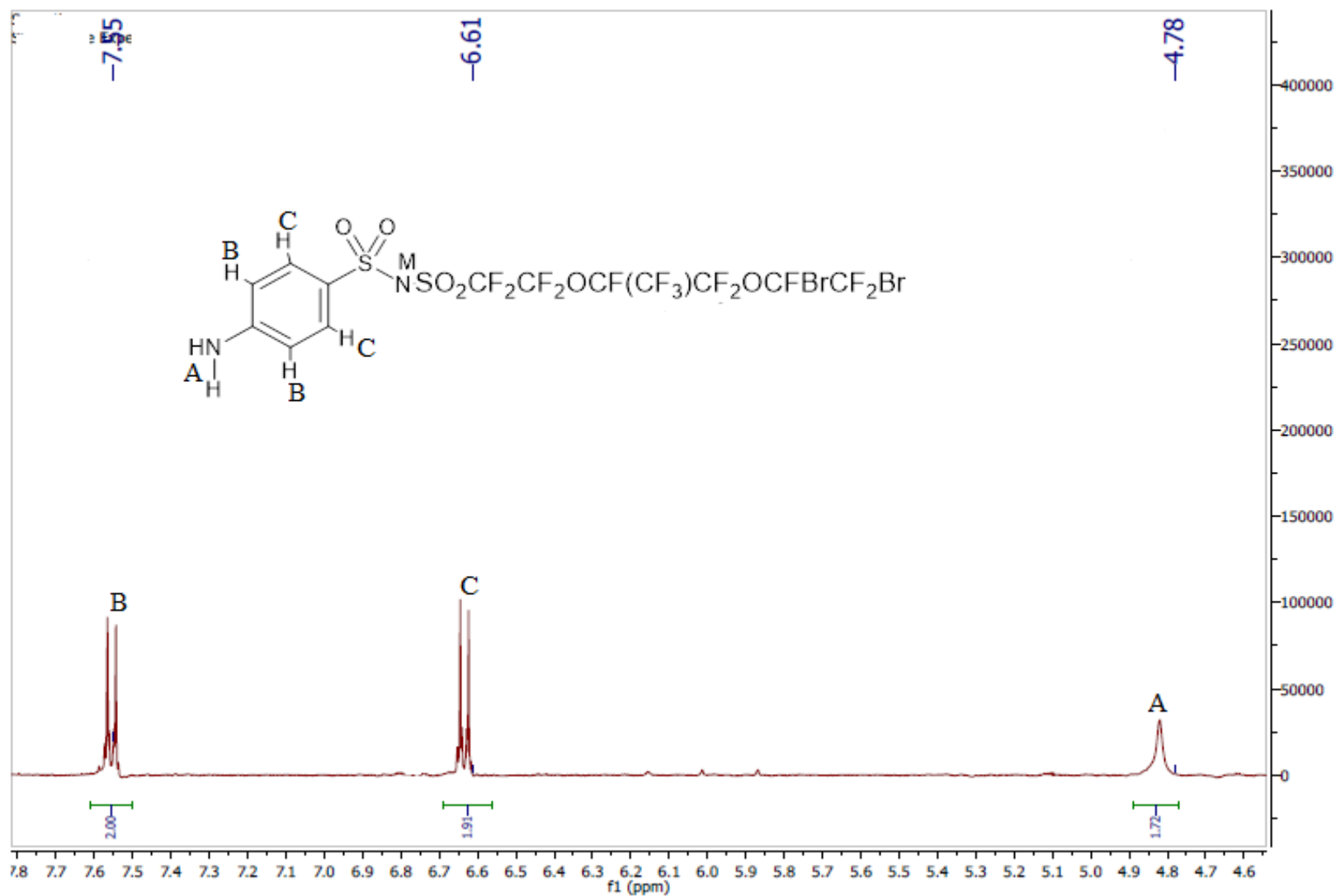
APPENDIX C5: Expanded ^1H NMR Spectrum of Compound **5**, 400MHz, CD_3CN



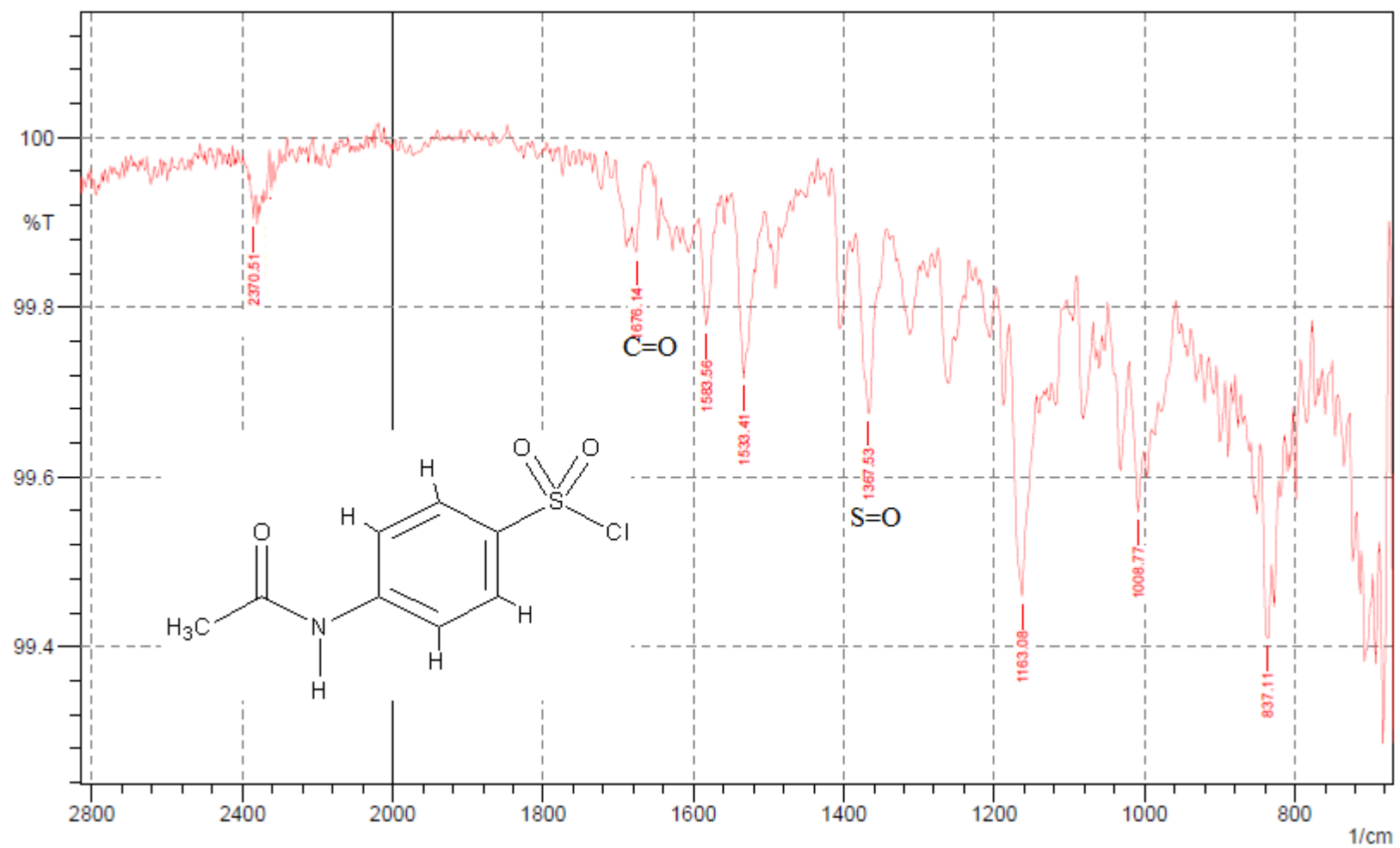
APPENDIX C6: ^1H NMR Spectrum of Compound **6**, 400MHz, CD_3CN



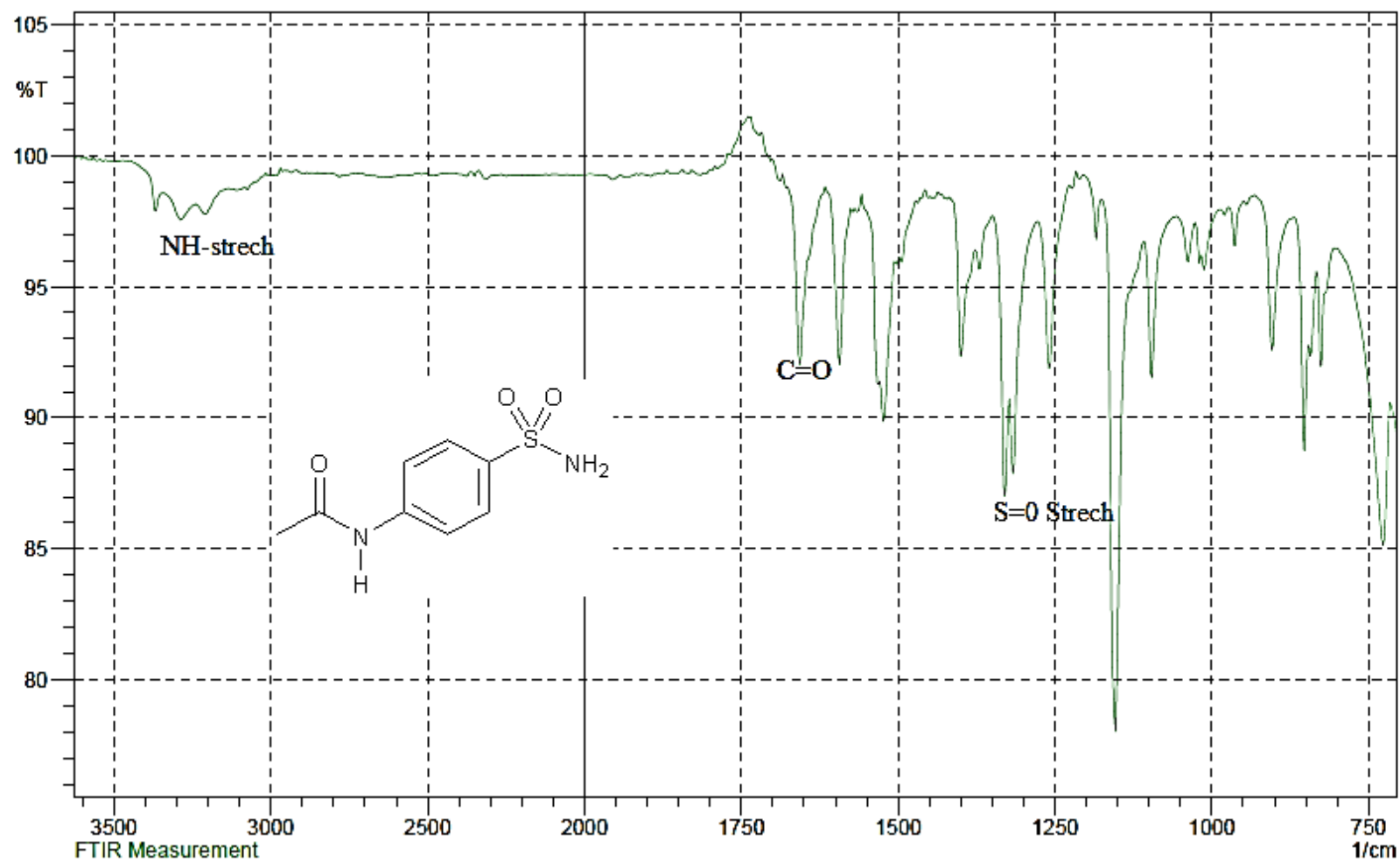
APPENDIX C7: Expanded ^1H NMR Spectrum of Compound **6**, 400MHz, CD_3CN



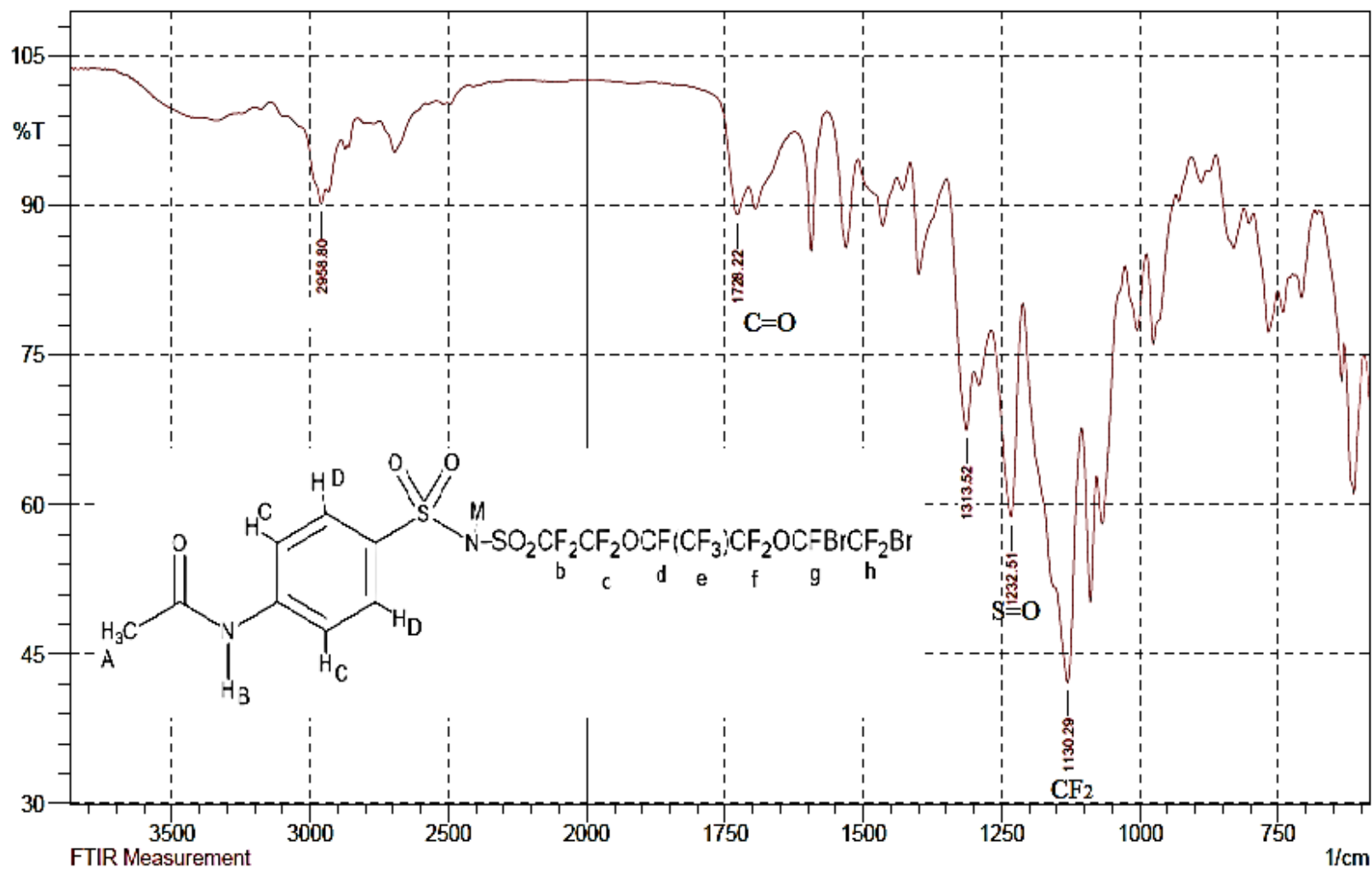
APPENDIX D1: FT-IR Spectrum of Compound 1



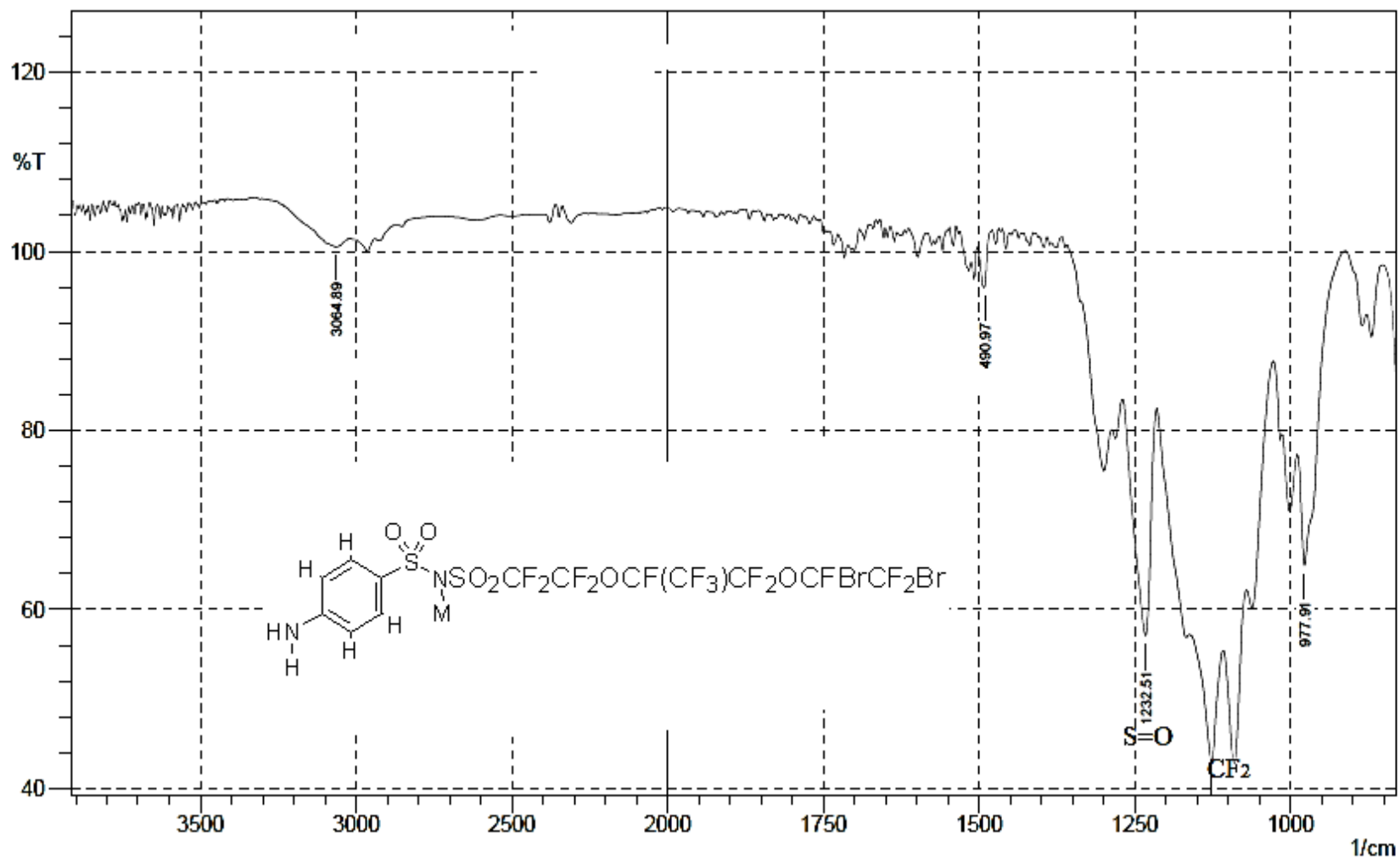
APPENDIX D2: FT-IR Spectrum of Compound 2



APPENDIX D3: FT-IR Spectrum of Compound 5



APPENDIX D4: FT-IR Spectrum of Compound 6



VITA

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- Barku, Y. A. V.; Abban, G. Phytochemical Studies, In-vitro Antibacterial Activities and Antioxidant Properties of the Methanolic and Ethyl Acetate Extracts of the Leaves of *Anogeissus leiocarpus*. *International Journal of Biochemistry Research & Review*. **2013**, 3(2), 137-145